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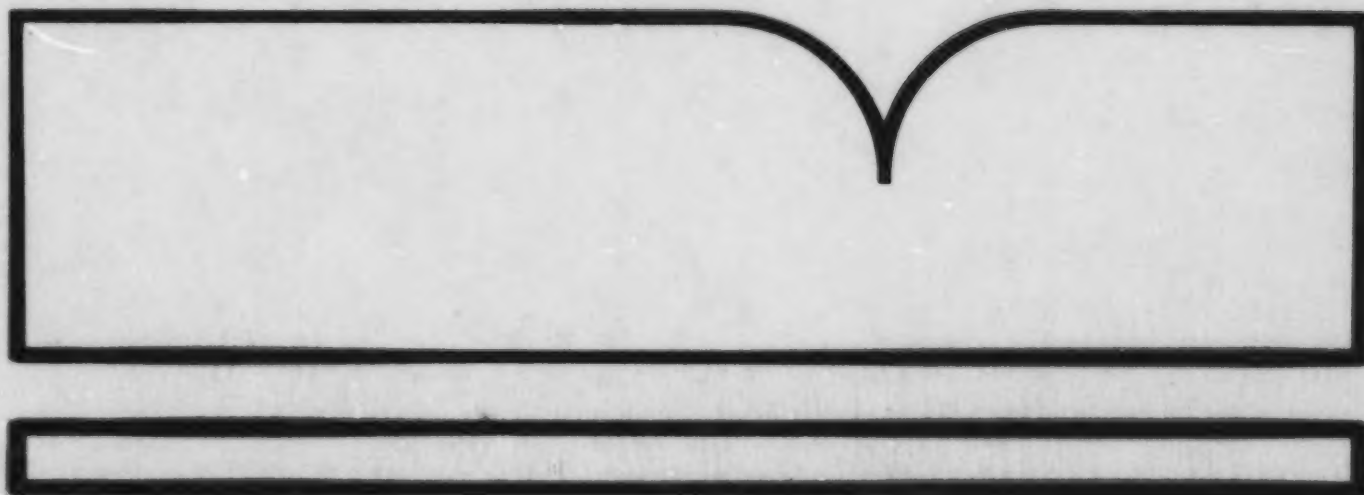
Local and Regional Contributions to
Urban Particulate Matter

Massachusetts Inst. of Tech., Cambridge

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LOCAL AND REGIONAL CONTRIBUTIONS TO URBAN
PARTICULATE MATTER

by

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ABSTRACT

This report summarizes the data analysis of two extensive field studies on urban particulate matter, the 1974-77 St. Louis (RAPS) and the July/August 1982 Philadelphia (PAFS) studies. Special emphasis is placed on the "dichot" measurements of particles that segregated the fine fraction ($<2.5\ \mu\text{m}$) and the coarse fraction ($2.5 - 15\ \mu\text{m}$ in St. Louis and $2.5 - 10\ \mu\text{m}$ in Philadelphia).

The major conclusion of this study is that in both cities the majority (more than 50%) of the total mass collected by the dichots is of regional, not local, origin. The regional share is about equally large for long-term (yearly, seasonal, monthly) and short-term (24-hours) averaging of concentrations. In the fine fraction, the regional component is even larger, 60% in St. Louis and 83% in Philadelphia. This conclusion is supported primarily by the observation that with the exception of a single site in both St. Louis and Philadelphia, all other sites within the extensive monitoring network, including remote rural sites, show a very low gradient of concentrations, indicating that the majority of collected aerosols does not originate from local sources, but must come from distant, regional sources that impact all monitors equally.

The annual average composition of PM-15 in St. Louis is 21% sulfate as SO_4 , 39% crustal matter (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO), 35% "unknown" (i.e., not determined by the routine analytical method, X-ray fluorescence), and 5% others (mainly trace metals). The summer monthly average composition of PM-10 in Philadelphia is 34% SO_4 , 14% crustal, 51% unknown, and 1% others. The unknown probably contains carbonaceous matter (elemental carbon and condensed organic matter, ammonium, nitrate, and water). Peak 24-hour compositions are not greatly different from the above.

Given the large proportion of regional contribution to and the chemical makeup of PM-10(15), neither dispersion nor receptor modeling based on local emission inventories and elemental composition are likely to accurately predict or interpret particle levels in urban airsheds.

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SUMMARY AND CONCLUSIONS

This report summarizes the findings of a two-year research effort on inhalable particle characteristics in urban airsheds. The research is based on data of two extensive urban field programs conducted by EPA, in St. Louis (1974-1977) and Philadelphia (1982). The St. Louis Regional Air Pollution Study (RAPS) was probably the largest monitoring effort ever undertaken to characterize the temporal and spatial characteristics of air quality in an urban environment, with special emphasis on inhalable particles. Among other monitoring devices, the RAPS campaign operated continuously 10 dichotomous inhalable particle samplers for over 3 years, covering an area of 30 X 90 km. In this study, one year of data (1976) was analyzed. The Philadelphia Aerosol Field Study (PAFS) was of shorter duration, 4 weeks in July/August 1982, and of smaller spatial extent--6 dichotomous samplers covering an area of 20 X 30 km.

While the two field studies were different in scope and extent, and even used different instrumentation and schedules, the main conclusion is the same: the majority (more than 50%) of the inhalable particle mass, whether averaged over a day, month, or year is not attributable to sources that lie within the metropolitan city limits, but is most likely due to regional sources.

This conclusion was reached in several ways:

1. Based on data from upwind or remote monitors in the network, the concentration of inhalable particles at these monitors amounted to more than 50% of the average mass at all monitors. It was not possible to attribute this common background to local sources; it is

much more likely that the background results from an influx of particles from outside the network boundaries.

2. In Philadelphia, where a more accurate emission inventory was available, dispersion modeling (using a state-of-the-art urban-scale dispersion model) can account only for 38% of the observed particle concentrations averaged over the 4 weeks of monitoring and the 6 monitoring sites. In St. Louis, dispersion modeling of sulfate particles could account only for 10-15% of the observed sulfate concentration.

3. Receptor modeling (multiple linear regression) in St. Louis allocated 34% of the annual average particle mass to sulfate, 49% "crustate" ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{Fe}_2\text{O}_3$), 7.4% vehicular emissions (Pb), 3.3% road salt (Cl), and 6.3% "others." In Philadelphia, due to limited data, receptor modeling is more uncertain; it allocated about 37% to sulfate, 29% crustate, a few percent each to oil/refineries, road salt, motor vehicles, and a potassium factor (agricultural dust?). In both cities, sulfate and crustate compose over 2/3 of the mass. Because of the long transformation time constant, of the order of a day, most of the sulfate particles must originate from distant (not local) sources. The crustate portion may consist of local fugitive dust, distant fugitive dust, and distant flyash from coal combustion. Thus, receptor modeling also indicates that a substantial portion of the inhalable particle mass may be of regional origin, although this type of modeling cannot quantify with certainty the local/regional apportionment.

4. A high-quality, long-term (16 months) inhalable particle monitoring effort was conducted in 1980/81 at 3 rural sites in the

Ohio River Valley (Shaw and Paur, 1983). The sites were specially selected so as not to be impacted by local sources. The 3-site, 16-month average concentration was about $30 \mu\text{g}/\text{m}^3$. This is higher than the 1976 St. Louis 10-site average annual background concentration, viz. $23 \mu\text{g}/\text{m}^3$, and similar to the 1982 Philadelphia, 6-site average monthly background concentration, viz. $34 \mu\text{g}/\text{m}^3$. It is conceivable that the inhalable particles, as found in the Ohio River Valley, permeate large regions of the eastern United States. The "regional" particle concentration probably provides the bulk of the urban "background" in St. Louis and Philadelphia.

Some other conclusions regarding inhalable particles in St. Louis and Philadelphia follow.

- o In St. Louis, the fine fraction (less than $2.5 \mu\text{m}$ diameter) and coarse fraction (2.5 - $15 \mu\text{m}$) masses are about equal; in Philadelphia the fine fraction ($<2.5 \mu\text{m}$) and coarse fraction (2.5 - $10 \mu\text{m}$) masses are about 3:1. (The dichot samplers had different inlets in St. Louis [up to $15 \mu\text{m}$ diameter particles] and Philadelphia [up to $10 \mu\text{m}$]).

- o In St. Louis, about 40% of the fine fraction consists of sulfate (SO_4); this percentage is even larger if it is assumed that most of the sulfate consists of hydrated ammonium sulfate. In Philadelphia, 43% of the fine fraction is SO_4 . The coarse fractions are dominated by crustal compounds (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , etc.).

- o In St. Louis, 24-hourly PM-15 concentrations exceeded $150 \mu\text{g}/\text{m}^3$ several times, which is the proposed lower range of the 24-hour PM-10 standard for particles. In Philadelphia, during the 4 weeks of monitoring, this range was approached ($147 \mu\text{g}/\text{m}^3$) only once at one site.

o The ratio of annual network averages of inhalable particle mass to total suspended particle mass is about 0.5 (± 0.15); however, the ratios of 24-hour averages may have a wider range, from 0.25 to 0.75. Short-term inhalable and total suspended particle concentrations are largely independent of each other.

o Dispersion modeling, at best, can account only for the local increment of inhalable particles; not the background that, as indicated above, appears to be of regional origin. Dispersion modeling requires an accurate emission inventory of inhalable particles (and their gaseous precursors), which cannot be obtained simply by assuming that there is a constant ratio of emissions of IP/TSP. The recently developed Particle Episodic Model (PEM) works quite well for the local increment, especially when modified for long-term (monthly, annual) and spatial (multi-site) averages, given an accurate emission inventory.

o Receptor modeling is only useful for the apportionment of those sources that have distinct compositions and are of local origin, e.g., vehicles, incinerators, metal processing industries, and oil-combustion-refining. Many sources have similar profiles and cannot be separated by receptor methods.

o The mass loading factor of elemental sulfur (sulfur-related mass divided by sulfur mass) is about 5 in St. Louis and about 4 in Philadelphia. This factor is larger than the stoichiometric factor of 3 for SO_4 , indicating that elemental sulfur carries along some other species, probably ammonium and water.

o A "mixed" dispersion-receptor model was developed in which multiple pollutants, source compositions, and dispersion model-derived

transfer coefficients were used. The mixed model is computationally very intensive but yielded some useful information. To reconcile Philadelphia model predictions with observations, it would be necessary to increase the estimated coarse-fraction area-source emission rate, and decrease the fine fraction. For point sources, estimated emission rates of oil-fired power plants and/or refineries should be increased; of coal-fired power plants--decreased. Incinerator emissions should also be increased.

SECTION 1

ST. LOUIS AND PHILADELPHIA AMBIENT INHALABLE PARTICLE DATA ANALYSIS

This section presents an exploratory analysis of particle data collected in two major field studies in St. Louis and Philadelphia. The analysis provides the basis for the modeling studies presented in subsequent chapters. In this chapter we present the particle concentrations and the elemental and chemical compositions.

In St. Louis, 10 particle monitors (dichots) were deployed over an area of 30 x 90 km (Figure 1). Several monitors (e.g., numbers 9 and 10) were located in rural areas. Data from calendar year 1976 are used (Strothman and Schiermeier, 1979). In Philadelphia, 6 particle monitors were deployed over an area of 20 x 30 km, one of which (Clarksboro) was in rural NJ (Figure 2). Data from a one-month period in July-August 1982 are used (Toothman, 1984). In both cities the sampling period was 12 hours. In St. Louis, the dichot coarse fraction cutoff was 15 μm (nominal); in Philadelphia, 10 μm . The fine fraction size cutoff was 2.5 μm in both cities.

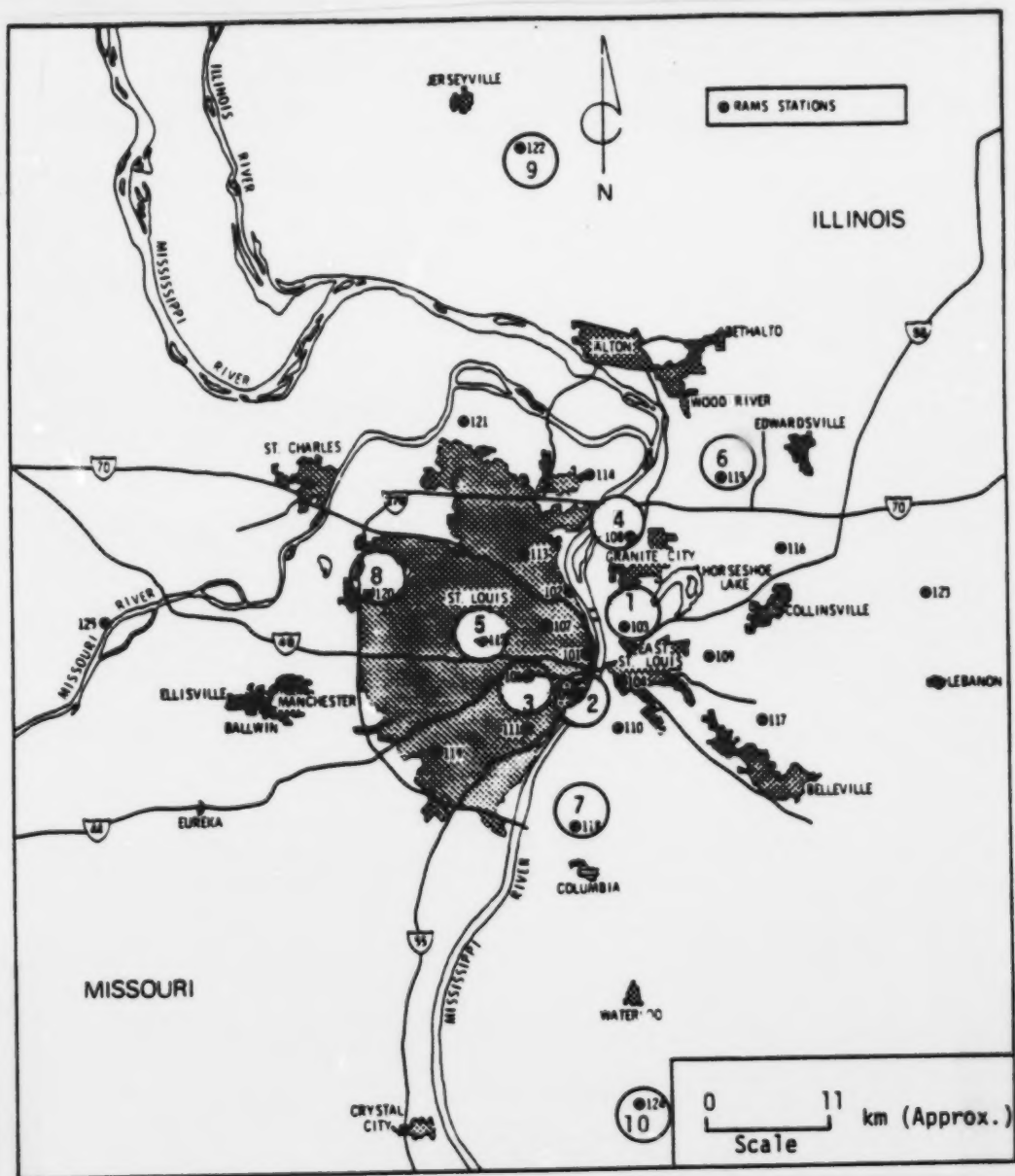


Figure 1. Location of monitors in the St. Louis area. Particle monitoring sites shown as numbers within large circles. Small numbers show original site number; location of 15 gas monitoring sites also are shown.

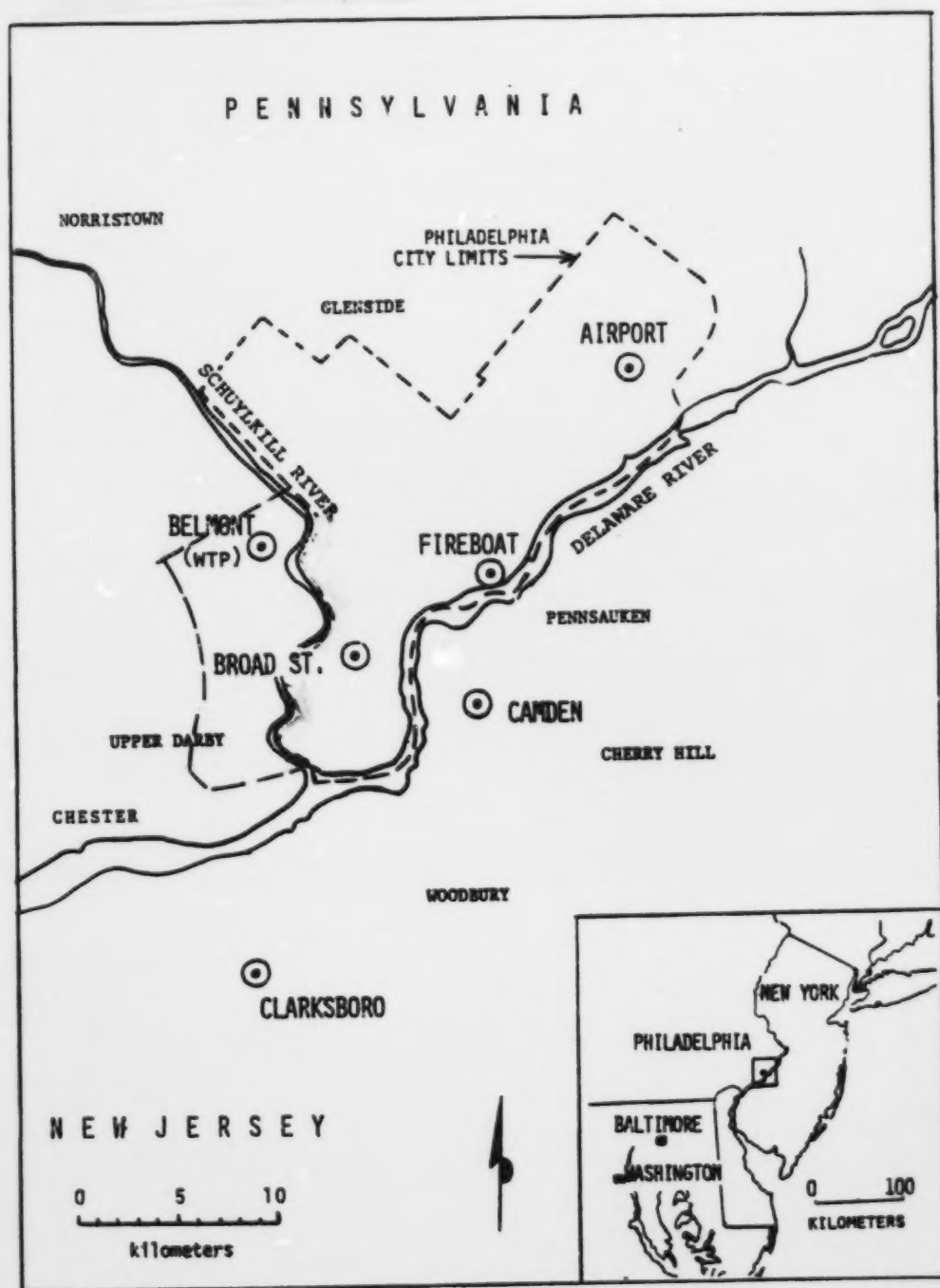


Figure 2. Location of monitors in Philadelphia. Monitor sites shown as circles.

1.1 Particle Composition

The annual average fine and coarse fraction concentrations at the ten particle monitoring sites in St. Louis, and the one-month average at three Philadelphia sites are listed in Table 1. In St. Louis, annual fine and coarse fraction concentrations are about equal, $20 \mu\text{g}/\text{m}^3$ each. In Philadelphia, the monthly fine fraction concentration is $27 \mu\text{g}/\text{m}^3$, the coarse, $9.2 \mu\text{g}/\text{m}^3$. The fine/coarse ratios have been different in the two cities for several reasons. First, the larger size cutoff for coarse particles in St. Louis ($15 \mu\text{m}$) may have collected more coarse particles compared to Philadelphia ($10 \mu\text{m}$). Also, in Philadelphia relatively higher concentration of fine particles may have occurred because most sulfate arrives in the fine fraction and sulfate concentrations are highest in the summer when the measurements were made. Third, Philadelphia may have had fewer fugitive coarse dust sources than St. Louis due to an effective dust control program.

In both cities many elements arrive in predominantly one size fraction: most S, V, Ni, Cu, As, Se, Br, Sn, and Pb are in the fine fraction, while most Al, Si, P, Cl, K, Ca, Ti, Cr, Mn, Fe, and Ba are in the coarse fraction. Only Cu and Sb have different size partitioning in the two cities. Several elements were not measured above the noise level, including fine and coarse As, Ga, Rb and Hg, and coarse Se, Sn and Sb.

While 29 elements were measured in St. Louis and 42 in Philadelphia, only a few elements compose the bulk of the aerosol. Table 2 lists the principal constituents and their oxidized form. Both annual average and summer levels are shown for St. Louis.

TABLE 1. AVERAGE CONCENTRATIONS AND PERCENTAGE OF ELEMENT IN FINE FRACTION FOR DICHOT VARIABLES IN ST. LOUIS AND PHILADELPHIA

	St. Louis			Philadelphia		
	concentration fine ₃ (ng/m ³)	coarse (ng/m ³)	fine fraction (%)	concentration fine ₃ (ng/m ³)	coarse (ng/m ³)	fine fraction (%)
	annual average			monthly average		
Mass	20200.0	20100.0	50.1	27095.4	9168.9	74.7
Al	119.4	914.1	11.6	32.4	407.8	7.4
Si	242.2	3355.6	6.7	92.6	1191.2	7.2
P	18.8	209.2	8.2	5.5	26.2	17.5
S	2602.6	284.2	90.2	3873.7	221.4	94.6
Cl	88.0	245.2	26.4	4.3	70.7	5.7
K	150.6	313.3	32.5	77.5	123.5	38.6
Ca	124.9	2269.9	5.2	33.9	281.9	10.7
Ti	28.0	147.6	15.9	10.7	44.8	19.3
V	3.0	2.3	56.6	14.3	6.3	69.5
Cr	4.9	7.4	39.8	2.2	2.8	44.1
Mn	18.8	26.6	41.4	5.2	8.3	38.4
Fe	172.7	873.0	16.5	76.7	364.2	17.4
Ni	2.7	2.4	52.9	8.0	3.0	72.8
Cu	20.1	7.0	74.2	2.0	2.8	42.0
Zn	89.1	53.9	62.3	57.0	24.0	70.4
Ga	0.1	0.2	33.3	0.1	0.2	40.0
As	2.0	0.8	71.4	0.2	0.2	50.0
Se	2.4	0.2	92.3	1.2	0.2	87.5
Br	104.2	21.3	83.0	22.6	11.8	65.6
Rb	0.4	1.1	26.7	0.3	0.6	37.0
Sr	0.6	5.0	10.7	0.6	1.7	24.6
Cd	3.6	1.1	76.6	1.5	0.8	66.7
Sn	6.6	0.7	90.4	4.4	1.9	70.0
Sb	2.6	0.8	76.5	20.5	48.6	29.7
Ba	7.7	20.9	26.9	2.9	7.5	28.0
Hg	0.5	0.6	45.5	0.1	0.1	50.0
Pb	461.3	125.1	78.7	198.6	41.1	82.9

TABLE 2. PARTICLE FRACTIONIZATION IN ST. LOUIS AND PHILADELPHIA

	element	elemental		compound	oxidized form			
		fine ₃ (ng/m ³)	coarse ₃ (ng/m ³)		fine fraction (ng/m ³)	(%)	coarse fraction (ng/m ³)	(%)
St. Louis annual average	Al	119.4	914.1	Al ₂ O ₃	225.5	1.1	1726.5	8.6
	Si	242.2	3355.6	SiO ₂	519.1	2.8	7190.6	35.8
	P	18.8	209.2	P ₂ O ₄	57.6	0.4	641.1	3.1
	S	2602.6	284.2	SO ₄	7807.9	38.6	852.5	4.2
	Cl	88.0	245.2	NaCl	145.1	0.7	404.0	2.0
	K	150.6	313.3	K*	150.6	.7	313.3	1.5
	Ca	124.9	2269.9	CaO	174.9	1.0	3177.0	15.1
	Ti	28.0	147.6	TiO ₂	46.8	0.2	246.5	1.2
	Fe	172.7	873.0	Fe ₂ O ₃	246.6	1.2	1246.6	6.2
	Pb	461.3	125.1	Pb*	461.3	2.5	125.1	0.7
	other	269.3	152.2	others	269.3	1.3	152.2	0.8
				unknown	10364.6	51.2	4176.7	21.4
	TOTAL	20200.0	20100.0	TOTAL	20200.0	100.0	20100.0	100.0
St. Louis monthly average (summer)	Al	147.9	1092.1	Al ₂ O ₃	279.4	0.9	2062.9	8.4
	Si	354.5	3988.9	SiO ₂	759.6	2.5	8547.6	34.6
	P	14.4	252.8	P ₂ O ₄	44.1	0.1	774.8	3.1
	S	4248.7	384.1	SO ₄	12746.1	41.9	1152.3	4.7
	Cl	77.6	184.4	NaCl	127.9	0.4	303.9	1.2
	K	176.3	365.9	K*	176.3	0.6	365.9	1.5
	Ca	132.2	2463.4	CaO	185.1	0.6	3449.5	14.0
	Ti	34.8	170.6	TiO ₂	58.1	0.1	284.9	1.2
	Fe	187.1	983.5	Fe ₂ O ₃	267.2	0.8	1404.4	5.7
	Pb	483.8	125.6	Pb*	483.8	1.5	125.6	0.5
	other	231.9	137.7	others	231.9	0.8	137.7	0.6
				unknown	15040.4	49.5	6090.4	24.7
	TOTAL	30400.0	24700.0	TOTAL	30400.0	100.0	24700.0	100.0
Phila- delphia monthly average (summer)	Al	32.4	407.8	Al ₂ O ₃	61.6	0.1	768.4	8.3
	Si	92.5	1191.2	SiO ₂	198.1	0.7	2554.6	27.7
	P	5.5	26.2	P ₂ O ₄	17.1	0.0	79.1	0.9
	S	3878.7	221.8	SO ₄	11694.5	42.9	665.3	7.2
	Cl	4.3	70.7	NaCl	6.9	0.0	114.7	1.2
	K	77.5	123.4	K*	76.8	0.2	123.4	1.3
	Ca	33.9	281.9	CaO	47.4	0.1	393.8	4.3
	Ti	10.7	44.8	TiO ₂	18.2	0.0	75.2	0.8
	Fe	76.7	364.2	Fe ₂ O ₃	109.2	0.4	519.2	5.6
	Pb	198.6	41.1	Pb*	198.0	0.7	41.0	0.4
	others	143.4	126.0	others	143.4	0.5	126.0	1.3
				unknown	14658.0	53.0	3745.0	40.7
	TOTAL	27229.1	9205.8	TOTAL	27229.1	100.0	9205.8	100.0

*One reviewer comments that a more appropriate listing for K and Pb would be some oxidized form. Considering the atomic weights, this would not alter the composition distribution appreciably.

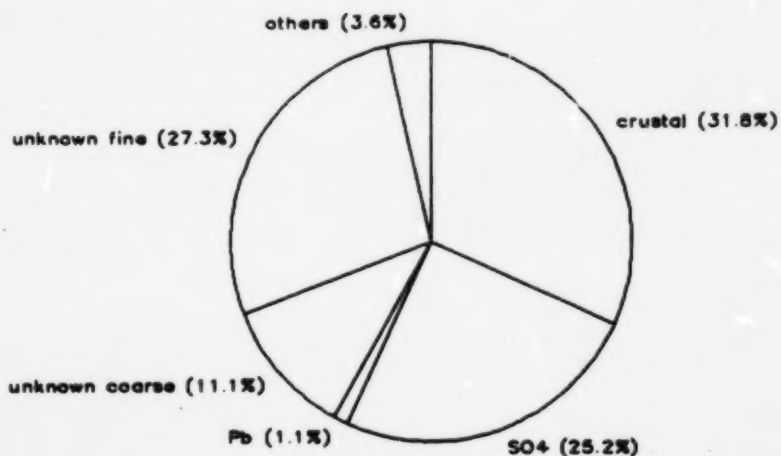
In St. Louis, 39% of the annual average fine fraction concentration is composed of SO_4 . Assuming S is in the form of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, this compound would account for 53% of the fine fraction. The coarse fraction consists mostly of crustal compounds. Measured elements account for 21 and 44% of the fine and coarse mass, respectively, or 49 and 79% assuming they are present as oxides. The remainder may be carbonaceous material (elemental carbon and organic compounds), water (hygroscopic and crystalline), and nitrogen compounds (NO_3 and ammonium). The water content may depend on seasonal and climatic factors.

The Philadelphia monthly average mass apportionment is similar to the summer monthly average apportionment in St. Louis. SO_4 accounts for 42% of the fine fraction mass. Oxidized frms of Al, Si, Ca, S and Fe account for most of the coarse fraction mass. A significant fraction of particle levels, 53 and 41% of the fine and coarse fractions, respectively, is unaccounted for in the mass apportionment.

The mass apportionment for combined size fractions is shown in Figure 3. Crustal elements Al, Si, P, K, Ca and Fe, are combined. Summer results in St. Louis are shown so that compositions in the two cities may be compared. SO_4 composes 34% of IP in Philadelphia and 25% in St. Louis. The crustal contribution is 32% in St. Louis and only 13% in Philadelphia. The mass apportionment shows that the bulk of the aerosol in both cities is made up of SO_4 , crustal material, and "unknowns" (carbonaceous matter, nitrate ammonium, and water). Much of the material is probably of regional origin, since concentrations are fairly uniform across the widely dispersed monitors (see Section 2).

PM-15 Mass Apportionment at RAPS Sites

summer 10 site average = 55.1 $\mu\text{g}/\text{m}^3$



PM-10 Mass Apportionment at PAFS Sites

1 month 3 site average = 36.4 $\mu\text{g}/\text{m}^3$

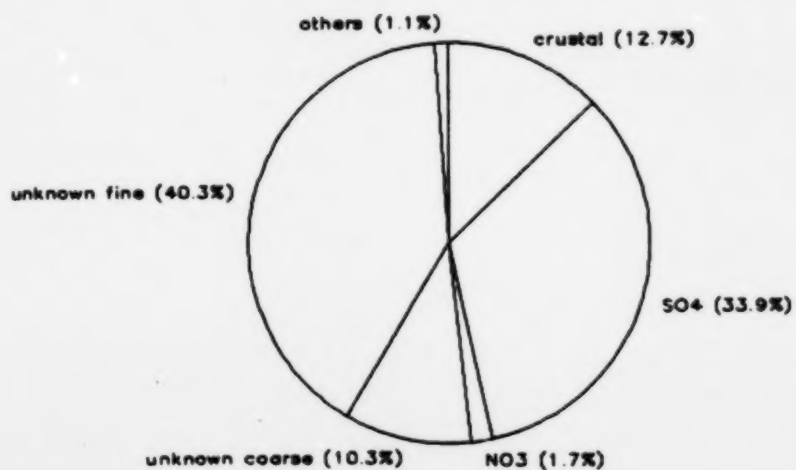


Figure 3. Mass apportionment in St. Louis and Philadelphia.

A comparison of total suspended particulate (TSP) and PM-10 mass is important because the proposed regulations set the frequency of PM-10 monitoring on the basis of known TSP concentrations, which have been measured using hi-vol samplers for many years at numerous locations (EPA, 1984). As TSP measurements include particles up to about 45 μ m in diameter, the comparison also helps to indicate the relationship between different size fractions.

Pace and Frank (1984) proposed a methodology for determining the probability of exceeding PM-10 standards utilizing frequency distributions of the PM-10/TSP ratios. The empirical analysis was based on data from 65 sites and 3 years (1980-82) from the EPA's National Inhalable Particulate Network. The derived average PM-15/TSP ratio is 0.55. The inter-quartile range (25th to 75th percentile) of annual average ratios is 0.48-0.62 and the extreme range (1st to 99th percentile) is 0.29-0.90. For 24-hour averages, the inter-quartile range of ratios is 0.46-0.63 and the extreme range is 0.21-0.92 (Meyer et al., 1984). Urban and rural sites have statistically different ratios. (The derivation of these ratios utilized simultaneous observations.)

Ratios of the annual average PM-15 to TSP concentrations at the 10 St. Louis sites are shown in Table 3. Ratios of 24-hour averages at the 90th and 95th percentiles, the second highest and highest observations, and the 10 site average are also shown. The short-term data use PM-15 and TSP samples that were not necessarily collected at the same time. It is seen that the shorter the averaging time, the greater the variability of ratios. The 10-site average annual ratio in St. Louis is similar to that determined by Pace and Frank (1984).

However, at the individual sites, the ratio varies between 0.47 and 0.63. (Average TSP concentrations ranged from 54 to 99 $\mu\text{g}/\text{m}^3$ at the 10 sites). For shorter-term averaging (at the highest concentrations), the ratio varies from 0.23 to 0.69. Low ratios may indicate a large amount of coarse dust collected in the peak TSP samples. (Peak TSP concentrations range from 152 to 483 $\mu\text{g}/\text{m}^3$.)

TABLE 3. RATIOS OF PM-15 TO TSP FOR 1976 AT THE 10 ST. LOUIS SITES

site	average	PM-15 to TSP Ratio percentile		second highest	highest
		90th	95th		
1	0.56	0.66	0.62	0.43	0.55
2	0.47	0.56	0.60	0.65	0.69
3	0.61	0.69	0.56	0.49	0.61
4	0.50	0.52	0.48	0.37	0.34
5	0.53	0.64	0.62	0.69	0.26
6	0.63	0.71	0.72	0.68	0.53
7	0.50	0.55	0.50	0.46	0.49
8	0.61	0.68	0.73	0.50	0.61
9	0.52	0.58	0.64	0.65	0.23
10	0.56	0.58	0.50	0.50	0.61
average	0.55	0.62	0.60	0.54	0.49

TSP and PM-15 observations are compared by regressing PM-15 (as the independent variable) on TSP. Results are shown in Table 4. While the slopes at most sites are close to unity, the intercept terms are large and equal about one-half of the annual average TSP concentration. The R^2 statistics show low correlation between the two variables. A pooled regression was not performed due to a lack of

homogeneity of variances at the sites.

TABLE 4. REGRESSION OF PM-15 ON TSP AT 10 ST. LOUIS SITES

Site	slope*	intercept*	R ²
1	0.90	49.4	0.33
2	0.94	50.3	0.43
3	0.96	32.8	0.44
4	1.15	38.9	0.26
5	1.52	14.9	0.53
6	1.01	21.3	0.53
7	0.96	35.8	0.28
8	0.61	34.1	0.21
9	0.86	33.1	0.13
10	0.86	28.1	0.22

*All coefficients are significant ($p < 0.01$) except the intercept for site 5 ($p < 0.03$). Approximately 120 observations at each site.

While not necessarily representative of other locations, the variation of the ratios and the large intercept terms in the regressions indicate considerable variation in the relationship between TSP and PM-15. Consequently, inferences of PM-10 levels from TSP measurements may be questionable.

1.2 Temporal and Spatial Correlation

Table 5 shows the highest 24-hour particle concentrations at each monitoring site. In St. Louis, the proposed PM-10 standard of 150 $\mu\text{g}/\text{m}^3$ was exceeded five times at site 1 and once at site 2. (Note that St. Louis dichots collected PM-15; therefore, PM-10

concentrations could be lower.) Other urban sites (3 and 4) experienced concentrations near the proposed standard. The highest concentration of $203 \mu\text{g}/\text{m}^3$ occurred at site 1 on June 9, 1976.

TABLE 5. HIGHEST 24-HOUR PM-15 CONCENTRATIONS IN ST. LOUIS AND PM-10 CONCENTRATIONS IN PHILADELPHIA ($\mu\text{g}/\text{m}^3$).

rank	St. Louis sites										Philadelphia sites					
	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6
1	203	157	146	141	128	123	96	116	105	90	79	70	74	79	147	73
2	155	149	124	126	125	112	94	103	96	75	68	69	67	68	108	72
3	154	147	117	116	121	103	93	92	95	67	68	67	63	65	101	71
4	153	132	108	107	118	99	88	90	94	63	66	64	57	55	95	70
5	152	132	107	105	113	97	86	84	94	61	64	59	53	55	82	69
6	147	130	104	104	109	95	81	77	82	60	62	59	49	55	78	64
7	146	129	97	101	98	89	76	74	76	58	61	58	49	54	77	62
8	146	120	97	99	97	87	74	73	75	58	55	55	47	53	75	55
9	142	119	96	96	96	86	73	72	74	57	53	51	44	51	73	55
10	132	116	95	94	94	85	70	72	71	55	51	51	44	48	73	50

In Philadelphia, all 24-hour PM-10 levels were below the proposed lower range of the standard. The highest PM-10 concentration ($147 \mu\text{g}/\text{m}^3$) occurred at the Fireboat station on July 28, 1982. The five highest concentrations occurred at this site, which was located near ongoing construction in an industrial area with heavy truck traffic. The Broad Street site had the sixth highest but substantially lower concentration of $79 \mu\text{g}/\text{m}^3$.

The highest concentrations at the 10 St. Louis sites generally occurred in the same time periods, as shown in Table 6. A total of 56 of these concentrations occurred in two summer periods (Julian days 232-238 and 159-162). The highest concentrations at all monitors occurred during these two periods, (except site 2), as well as the

second highest concentrations at all monitors (except site 6). High concentrations in Philadelphia are also "clustered." Many of the highest concentrations occurred during July 26-28 and August 4-5, 1982. A similar analysis was performed for the lowest particle concentrations. Many of the lowest concentrations in both cities are also clustered into short time intervals, although the simultaneity is less pronounced.

TABLE 6. NUMBER OF HIGHEST CONCENTRATIONS WITHIN SPECIFIED DATES

Julian day	month & day	-----site number-----									
		1	2	3	4	5	6	7	8	9	10
232-238	8/21-27	1	5	5	1	3		3	5	1	6
159-162	6/9-12	4	3	2	2	2	3	4		6	*
97-98	4/8-9				2	2			1		1
275-276	10/3-4	2	2	*			1				*
186-190	7/6-10				1	2	2				
321-322	11/18-19			*			1	1	1		*
183	7/3	1					1				
Other dates		265		147	258	199	240	318	231	240	147
		174		133	262		247	259	204	178	142
				201	121				262	125	133
					226						

*Missing data.

The correlation between pollutant variables at different monitoring sites provides another measure of the degree of association or simultaneity. Table 7 lists the inter-site correlation for several variables in Philadelphia; the average correlation between the six receptors is shown. Fine fraction mass and SO_4 concentrations have correlation coefficients averaging 0.8 between monitoring sites. Thus, about 65% of the variance of these pollutants is common to all sites, attributable to factors that similarly affect pollutant levels at all sites, i.e., the regional component and meteorology. SO_2 and

coarse fraction concentrations have lower correlation; less than 15% of the variance is common. Correlations in St. Louis show similar patterns.

TABLE 7. STATISTICS OF INTER-SITE CORRELATION IN PHILADELPHIA

	average	minimum	maximum
fine mass	0.82	0.68	0.93
coarse mass	0.43	0.01	0.68
fine SO ₄	0.80	0.55	0.97
SO ₂	0.26	-0.27	0.76

The coefficient of variation (COV) provides an indication of the spatial variation of long term pollutant levels in the monitoring network. Table 8 shows COVs, calculated as the ratio of the standard deviation of annual average concentrations to the average concentration at the 10 St. Louis monitoring sites. COVs are under 25% for mass, S, Si, and Se. Thus, concentrations of these variables may vary relatively little across the network. As shown later (e.g., using pollutant roses), these variables have similar concentrations at both urban and rural locations. Sites 9 and 10, the southernmost and northernmost locations, have the lowest concentrations of most variables, with levels lower by about one standard deviation of the variability at the 10 sites. Conversely, sites 1 and 2, in the center of St. Louis, have the highest concentrations of most fine fraction pollutants; site 1 also has the highest level of most coarse fraction variables. Thus, local sources produce higher levels at center city sites. This "urban increment" is quantified in Section 2.

TABLE 8. COEFFICIENT OF VARIATION FOR DICHOT VARIABLES
(percent)

var.	--St. Louis--		-Philadelphia-	
	fine	coarse	fine	coarse
Mass	16	25	5	19
Al	29	24	20	26
Si	26	19	20	25
P	50	55	33	13
S	9	41	3	17
Cl	80	47	115	32
K	29	30	23	17
Ca	27	29	28	27
Ti	86	74	32	29
V	43	57	24	21
Cr	45	55	28	34
Mn	98	50	25	23
Fe	42	44	22	28
Ni	43	51	22	20
Cu	68	62	31	41
Zn	42	65	41	27
Ga	50	34	35	na
As	39	74	75	28
Se	16	44	8	28
Br	57	63	30	27
Ru	54	28	37	8
Sr	43	34	8	22
Cd	41	71	13	12
Sn	53	114	21	17
Sb	74	53	104	113
Ba	81	57	15	22
Hg	44	58	82	82
Pb	42	47	24	28

1.3 Concentrations by Wind Direction

Several methods are evaluated to determine the effect of wind direction during the 12-hour dichot sampling periods: (1) using the resultant wind direction during the 12-hour sampling period; (2) using only samples for which the 12-hour directional variability (defined as circular dispersion) was less than 10, 20, and 40 degrees respectively; and (3) using the hourly wind direction and dividing the sample mass into the wind sectors prevailing during the 12 hours (assuming constant pollutant flux in each sector). Restricting wind variability to 10 degrees eliminates 85% of the observations. With all but the most stringent directional criteria, methods (1) and (2) give comparable results. Method (3) obscures directional effects. Despite these differences, there is little sensitivity to the choice of method in the determination of average annual directional effects.

In St. Louis, 12-hour concentrations at each receptor are classified into 16 sectors by the prevailing wind direction. Sampling periods with directional variability greater than 40 degrees (approximately 15% of observations) are eliminated. Pollutant roses are used to portray the stratified concentrations. Figures 4 and 5 show roses for 20 fine fraction variables and 10 coarse fraction variables. The rose for each receptor is located at its UTM coordinates. (The UTM or Universal Transverse Mercator projection is a rectangular grid scaled in kilometers.) The length of the arms of each rose represents the average concentration with winds blowing from a given sector. Roses "point" to the emission sources which produce higher pollutant concentrations at a receptor.

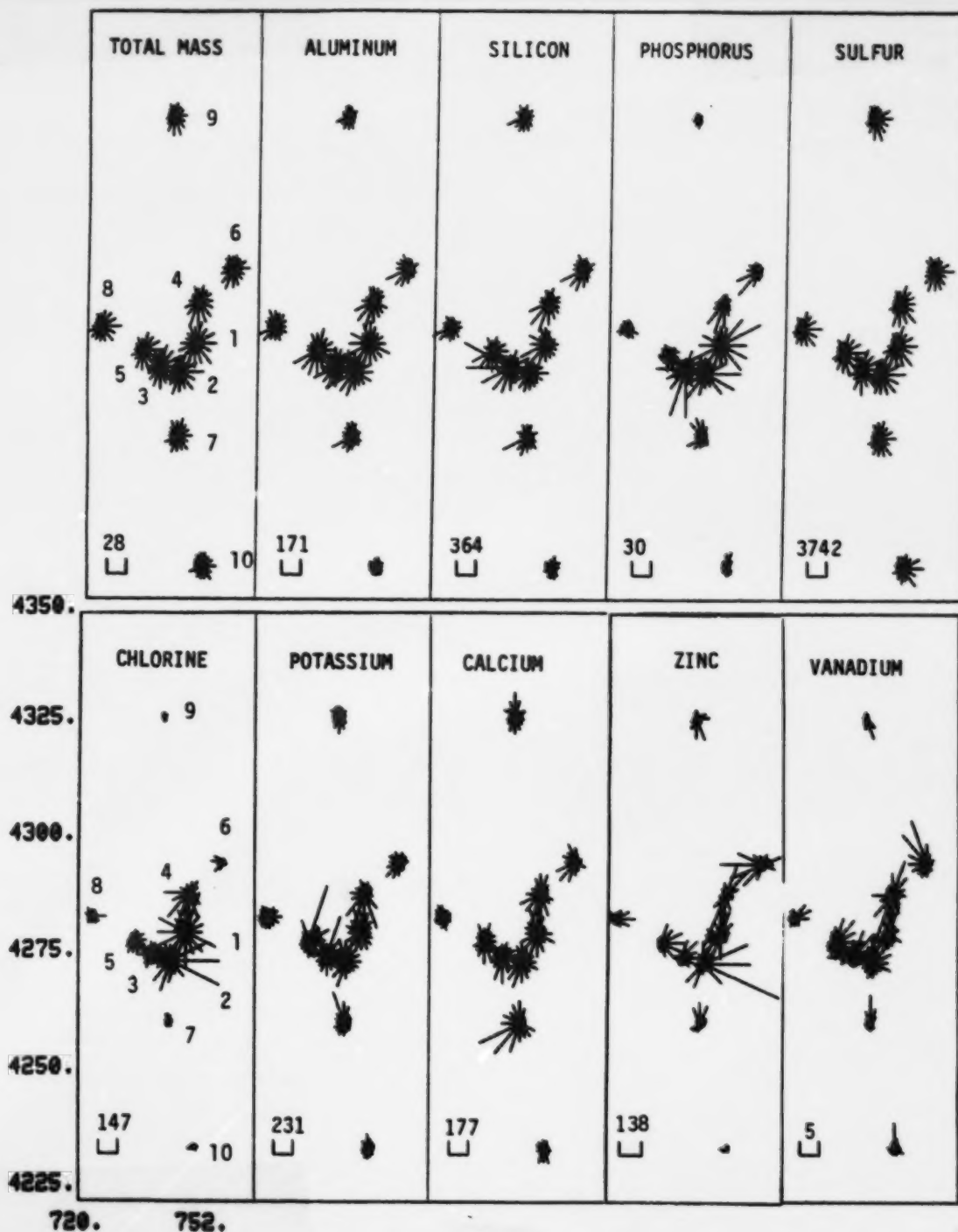


Figure 4. Annual pollution roses for fine fraction variables in St. Louis. Numbers indicate site number. Scales indicate concentrations in ng/m^3 , except total mass, in mg/m^3 . UTM coordinates on axes.

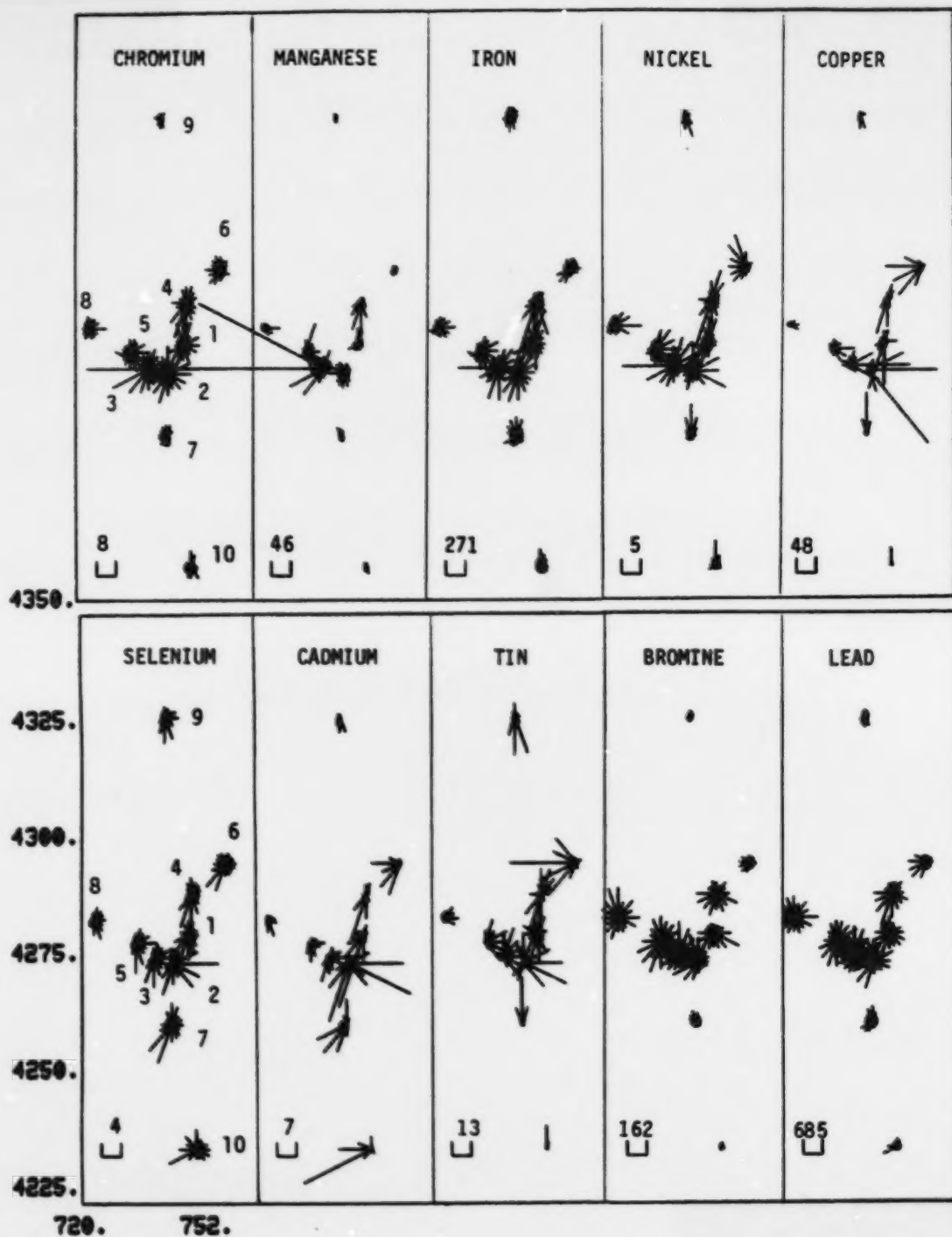


Figure 4. (continued)

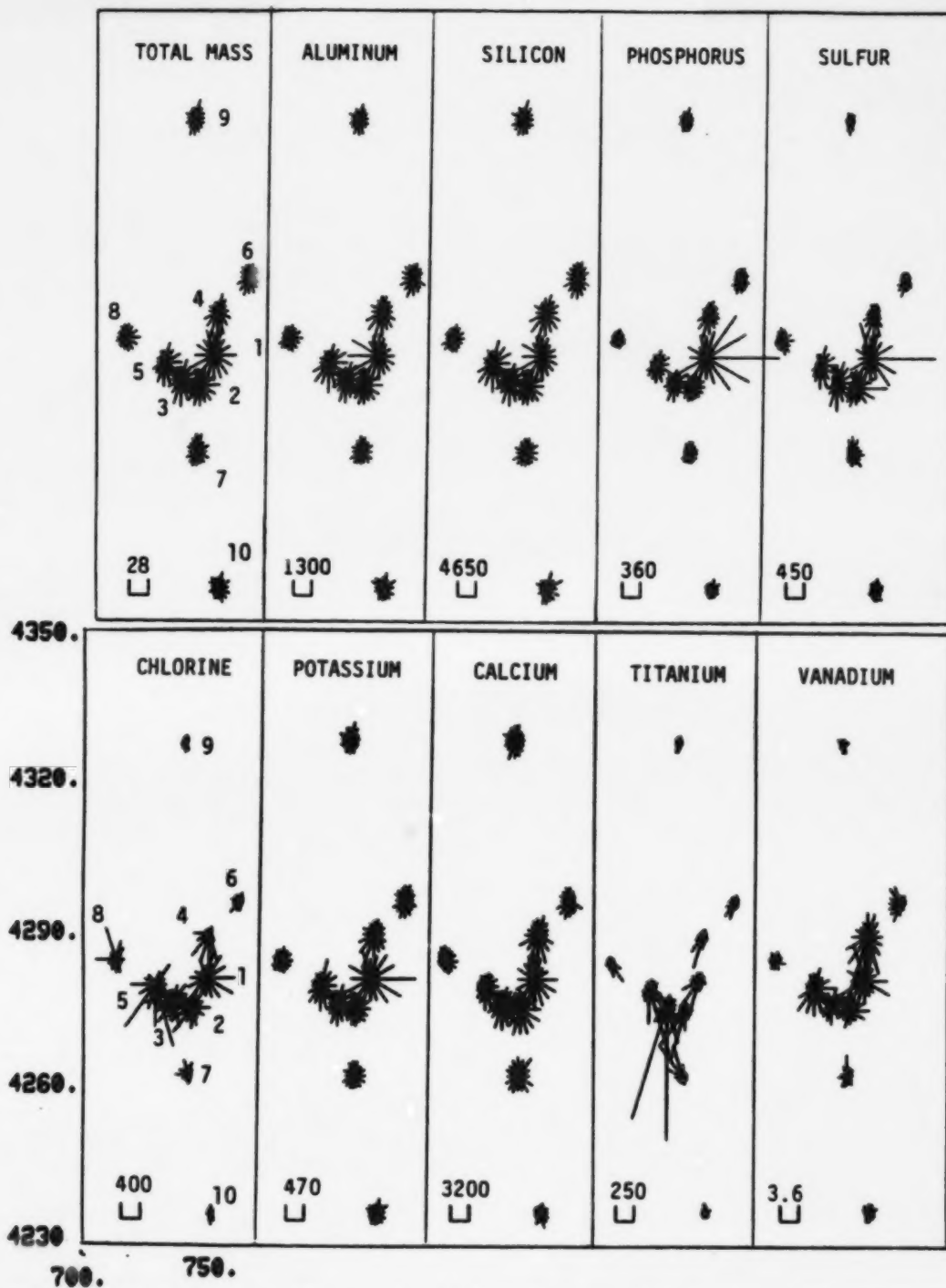


Figure 5. Annual pollution roses for coarse fraction variables in St. Louis. Otherwise as Figure 4.

The roses show vivid directional effects for several fine and coarse fraction metals, such as Ti, V, Ni, Cu, Cd, Sn and Zn. In contrast, mass, Al, Si and S display fairly uniform or isotropic distributions, with the exception of the Si rose at site 3. This site also has a very sharp and unique rose for Mn. Coarse fraction S at site 1 also displays large directional effects.

The pollutant roses indicate the relative concentrations at the 10 monitoring sites. In comparison to urban sites, rural sites have very low concentrations of most trace elements. This pattern suggests that urban sources emit most of these pollutants. In contrast, Al, Si, S, K and Ca concentrations are very similar at rural and urban sites, suggesting that these elements are of regional origin.

Figure 6 shows the location of major industrial facilities in St. Louis. (The figure does not include the northernmost and southernmost particle monitors.) A number of the pollution roses clearly point to specific emitters, especially if the emissions contain distinctive tracers. The following sources can be readily identified:

A paint factory located just south of the city is the major source of both fine and coarse fraction Ti (Rheingrover, 1977).

Two refineries to the NE of the city are the probable sources of fine fraction V, especially noticeable at sites 6 and 9.

A primary Zn smelter is indicated just E of monitor 2.

An iron works 1 km W of monitor 3 is the likely source of Mn.

Iron, steel and smelter industries are indicated by the highly directional roses for Ni, Cu, Cd and Sn. The roses point towards several clusters (SE and SW of St. Louis) of these industries. More specific information about source profiles is necessary to decompose these sources.

The density of vehicular traffic is reflected in the similar Br and Pb

roses.

Winter salting on high volume high speed roads is indicated by the coarse Cl roses. Roses at sites 1, 3, 5, 6 and 8 are oriented to nearby interstate highways 40, 56 and 70. (The coarse Cl roses exhibit a different pattern than fine Cl, Br, and Pb roses.)

Fine Cl roses at sites 1, 2 and 4, indicate a possible source of Cl near the Mississippi River.

A fertilizer plant just east of site 1 is indicated by the coarse P and K roses.

The S and fine mass pollutant roses are similar, which is expected since SO_4 composes much of the fine mass. Most of the SO_4 is probably derived from both local and regional coal combustion. The two largest local SO_2 point sources are the Union Electric Company facility 60 km SW of the city (UTM coordinates 688.8 and 4270.2) and the Illinois Power Company plant 106 km to the SW (UTM 775.7 and 4232.5). (Both facilities are beyond the scale of Figure 6.) These coal power plants have tall stacks, 213 and 184 m, respectively, and SO_2 emission rates several times larger than other local sources.

Coal flyash contains a number of trace compounds, including Si, Ca, Al, As, Se, and Pb, elements which are also emitted by other source classes. Se is emitted in relatively smaller quantities by other sources and thus is one of the better tracers for coal related aerosols. The Se roses are unusual in that they appear to be composed of two parts: a low level isotropic component of approximately equal magnitude at all sites, and a higher level component to the southwest, in the direction of the power plants. Roses for several other constituents of flyash, e.g., fine Al, Si, Ca and to some extent Cl,

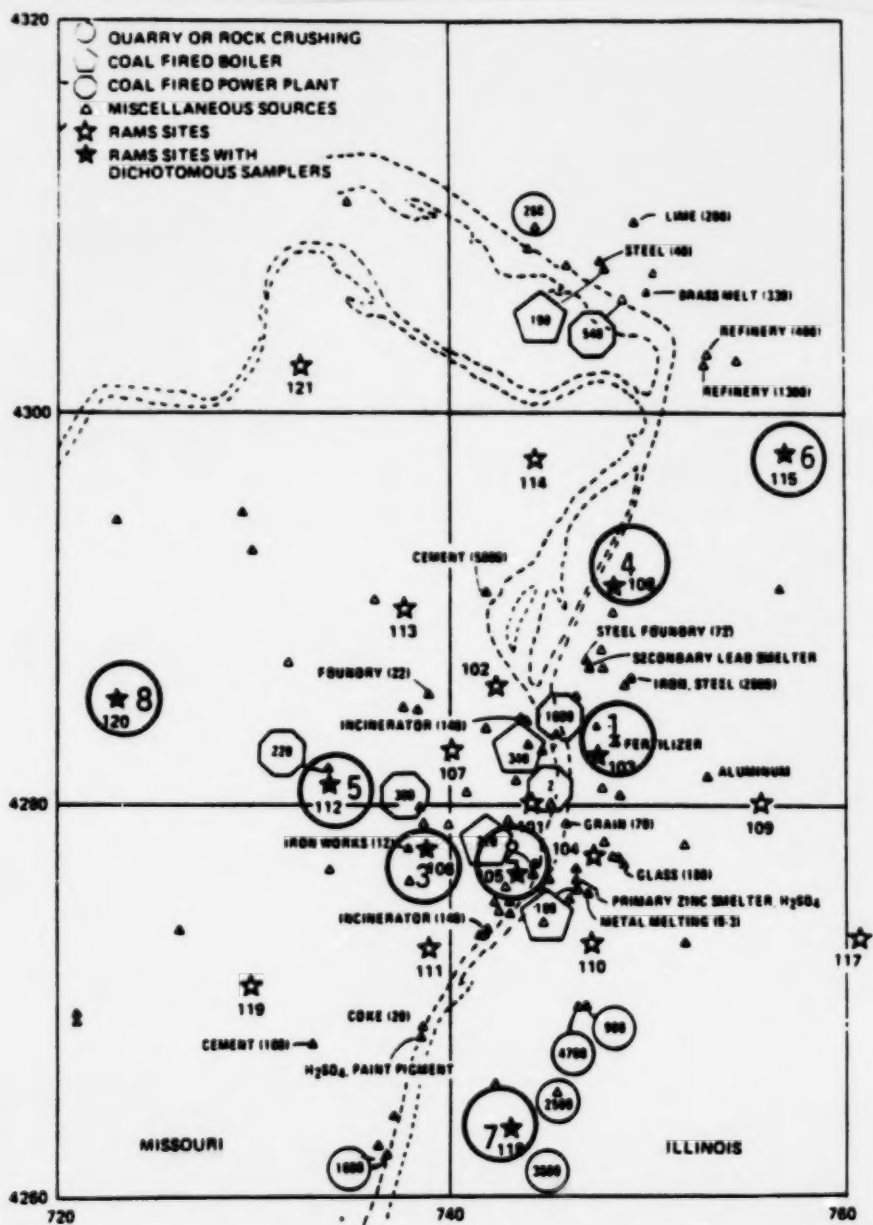


Figure 6. Location of monitors and major emission sources in St. Louis. Numbers in large circles indicate monitor sites. Emission rates are shown in tons per year in parentheses or within the symbols for selected sources. From Dzubay (1980).

show similar effects and suggest contributions from the power plants. However, the orientation of the fine mass and S roses is from the east, in the direction of the Ohio River Valley area, where many large coal-fired facilities are located.

Pollution roses are also developed for the three monitoring sites in Philadelphia where elemental measurements were made. Fine and coarse fraction roses for 20 elements are shown in Figures 7 and 8, respectively. Roses show concentrations observed at the Airport, Camden and Clarksboro sites, from NE to SW (top to bottom). Due to the fewer observations available, roses are calculated for only eight sectors. However, the roses show only seven arms, as the prevailing 12-hour wind never blew from the SE during the one month study period.

Fine fraction roses for mass and S are very similar. These roses are oriented to the SW, in the direction of prevailing winds and major source regions. Roses for K, Ti, V, Cr, Ni, Cu, Zn, Ba, and Sb indicate local sources in the Philadelphia area. The Mn, Fe, and Pb roses are similarly shaped, indicating vehicular and crustal sources which are well distributed in the area.

In the coarse fraction, roses at the three sites have similar shapes for each element, although the shapes vary depending on the element. Roses for mass and crustal elements Al, Si, P, S, K, Ca, and Fe are similar and again indicate an isotropic distribution of sources. Roses for Cl, V, Cr, Ni, Zn and Sb are different from the other coarse fraction roses and generally closely resemble the fine fraction roses for the respective elements.

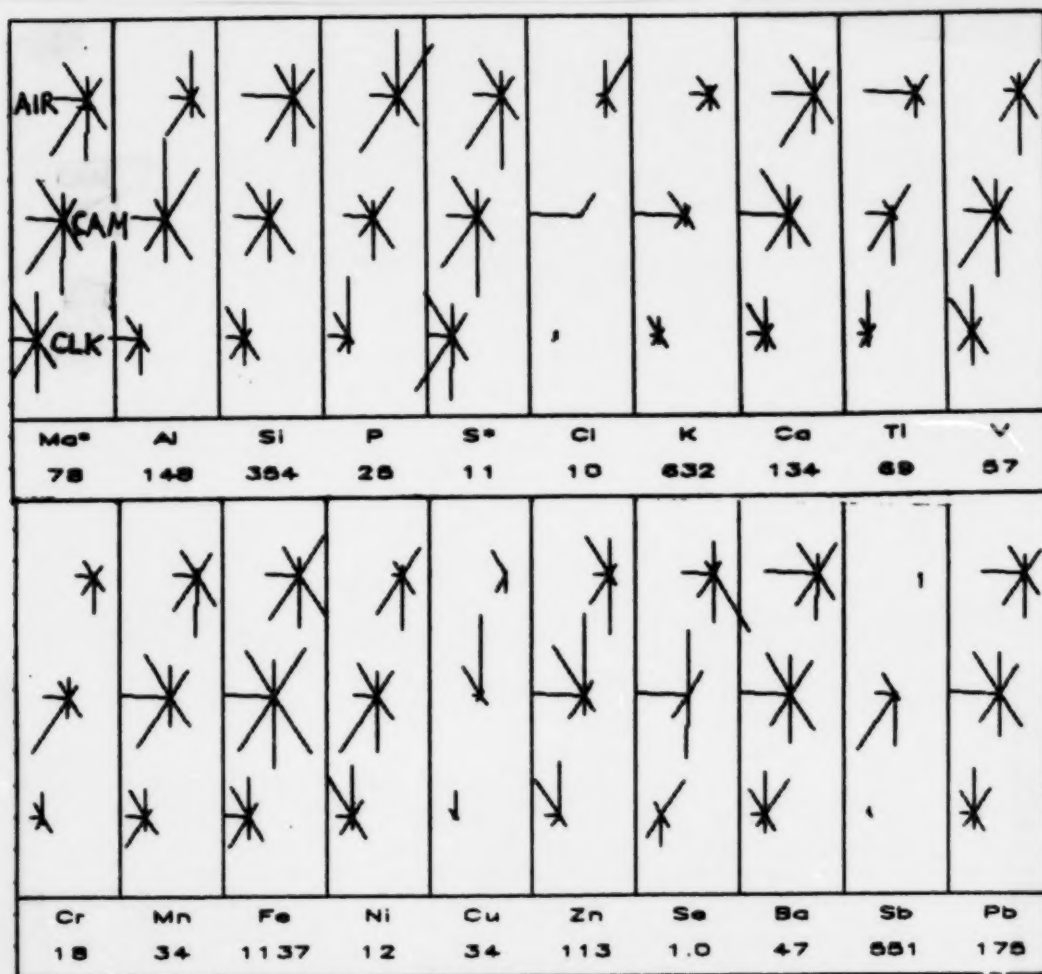


Figure 7. Pollution roses for fine fraction variables in Philadelphia. "Ma" represents total mass. Numbers indicate concentrations of longest arm, in ng/m^3 except for asterisk, in $\mu\text{g}/\text{m}^3$.

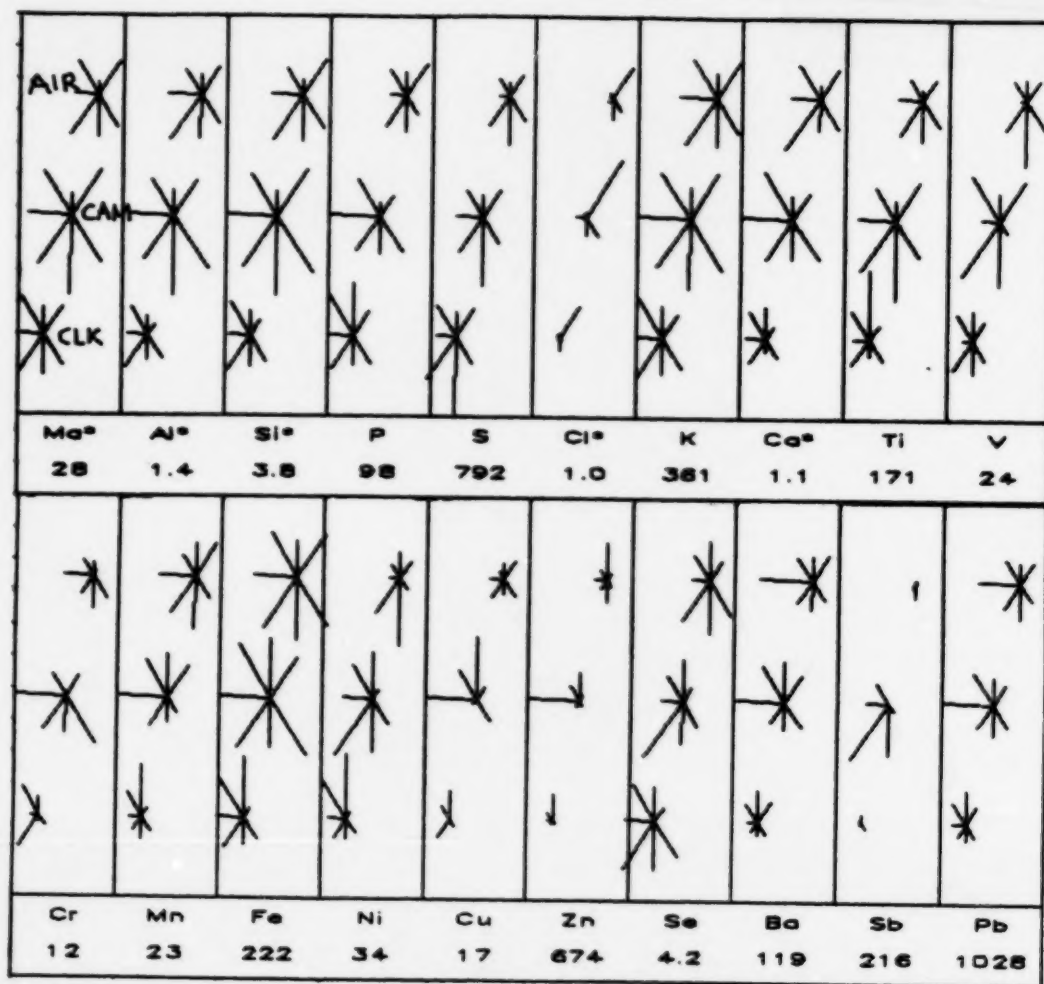


Figure 8. Pollution roses for coarse fraction variables in Philadelphia. Otherwise as Figure 7.

In comparison to St. Louis, it is difficult to identify individual emission sources in Philadelphia. The Philadelphia area contains many more emission sources that are difficult to pinpoint with only three monitoring sites. Furthermore, the available data do not permit fine directional resolution. While on average 7 observations compose each arm of the roses, as few as 3 observations are used for the NE and SE arms. Thus, the representativeness of the roses is limited.

1.4 Discussion and Summary

High PM-10 and PM-15 levels generally result from large contributions of both fine and coarse size fractions. While fine and coarse fractions are about equal in St. Louis, in Philadelphia the fine fraction is dominant at most sites. Based on the different compositions and low correlations, the two size fractions appear to have largely separate origins.

About one-half of the fine fraction particles and one-third of PM-10 consists of SO_4 . SO_4 levels are highest in the summer, probably due to the faster oxidation of SO_2 to SO_4 associated with increased photochemical activity, high temperatures and high humidities. At most urban and rural sites, concentrations of fine fraction mass and SO_4 are similar and their pollutant roses are nearly identical; both imply the importance of regional sources. At high concentrations, the fraction of trace metals, indicative of local sources, increases in St. Louis but decreases somewhat in Philadelphia, possibly due to the dominance of regional SO_4 in the latter city.

Coarse fraction particles contain large amounts of Al, Si, Ca, Fe and Mn and appear to be largely of crustal origin. This crustal

material composes a relatively constant fraction of the aerosol. On average, coarse fraction levels in Philadelphia are much lower than in St. Louis (summer averages of 9 vs. $25 \mu\text{g}/\text{m}^3$), probably due to the change in sampler design, which excludes larger particles. Source differences between the two cities may also be important. The highest coarse fraction concentrations occur during dry and dusty periods; concentrations tend to decrease during prolonged or heavy precipitation.

Other important findings of the exploratory analysis include:

In the one month of monitoring in Philadelphia, PM-10 levels at one site approached the proposed 24-hour standard of $150 \mu\text{g}/\text{m}^3$. In the one year period in St. Louis, PM-15 levels at several sites exceeded $150 \mu\text{g}/\text{m}^3$ six times.

The highest concentrations are associated with winds from the direction of major pollutant sources. In St. Louis, easterly wind probably bring large regional contributions, especially SO_4 from the Ohio River Valley. In Philadelphia, southwesterly winds bring the highest levels.

Particle levels at different sites are highly correlated, especially in the fine fraction. Many of the highest particle concentrations at different sites occur during the same time periods. However, the low correlation between fine and coarse fraction levels show the two fractions are largely independent.

Oxidized forms of the available elemental measurements account for about half of PM-10 levels in both cities. The remainder may be carbonaceous material, water and nitrogen compounds. The mass apportionment using the oxidized forms does not identify the source of the bulk of the aerosol.

Annual average PM-15/TSP ratios range from 0.47 to 0.63, in good agreement with measurements from the national monitoring network. However, 24-hour averages show a much wider range of ratios; short term PM-15 and TSP concentrations are largely independent of each other.

Particle concentrations are generally inversely related to wind speed and mixing height, although the effect is small and not consistent. Even small amounts of precipitation (0.05-0.1 inch) decrease fine and especially coarse fraction particle levels.

Many emission sources can be located using pollutant roses derived from 12-hour aerosol samples. Roses for Ti, V, Ni, Cu, Cd, Sn and Zn show strong directional effects, probably pointing to local sources. In contrast, Al, Si, Ca and S concentrations are nearly isotropically distributed, probably pointing to regional sources.

SECTION 2

LOCAL AND REGIONAL COMPONENTS OF PARTICLE CONCENTRATIONS

2.1 Introduction

Because particles are formed and transported over long distances, both local and regional or distant emission sources contribute to ambient particle concentrations. Thus, particle concentrations may be viewed as the sum of contributions from local and regional emission sources. The regional component of the total particle mass collected at a receptor is termed "background." Hereafter, "regional component" and "background" are used interchangeably. Local sources, situated within the airshed, produce concentration levels which generally increase toward the sources. This is the "urban increment." The regional or background component arises from the long range transport of pollutants into the airshed and attains about equal levels at all locations within the airshed. Local and regional particle concentrations need to be determined at both short and long averaging times, in accordance with the proposed PM-10 regulations.

The concentration $C_i(t)$ at observed at location i and time t may be modeled as

$$C_i(t) = L_i(t) + D(t) + V_i(t) \quad (1)$$

where $L_i(t)$ is local source contribution, $D(t)$ is the mean regional component which is constant in space on the urban scale, and $V_i(t)$ is

the measurement error. Assuming $V_j(t)$ is negligible, the following approaches may be used to separate local and regional components. Short range physical simulation (dispersion) models can estimate local contributions $L_j(t)$ by predicting concentrations in a "dense" receptor grid, which includes locations where high concentrations are expected. Regional levels $D(t)$ can be estimated using long range dispersion models. Regional levels can also be determined using observations from upwind or isolated monitoring sites.

The key disadvantage of using dispersion models is the uncertainty of predictions, which typically is a factor of two for short term averages (American Meteorological Society, 1981). In addition, this approach requires the availability of a suitable model, an accurate source inventory, and meteorological observations for a representative period, which is usually three years. Background may also be estimated as the average of concentrations recorded at several sites excluding those sites which could be impacted by specific local sources (EPA, 1984). If there are no monitors in the vicinity of the source, monitoring at a "regional" site is suggested. A regional site should be located away from the area of interest and not affected by local sources. For multi-source or urban areas, EPA suggests using an upwind or regional monitoring site.

The assumption of the recommended procedures is that the upwind or regional monitoring site receives the lowest concentration in the monitoring network. In both rural and urban areas, the local increment or contribution is the difference between the highest and lowest concentrations.

Estimating regional and local contributions of PM-10 in urban

areas may be difficult for several reasons. First, high particle concentrations have been observed across broad areas (e.g., Shaw and Paur, 1983); thus the regional component may compose a large fraction of particle levels. Second, since particles are emitted by many sources and particle collection periods are relatively long (12 to 24 hours), wind shifts during the collection period may invalidate the designation of particular sites as "upwind." Third, few urban areas have had extensive monitoring of small particles. At present, most urban particle networks measure TSP, not PM-10, and only at a few sites within an urban airshed. Measurements are usually rendered only every sixth day. In these instances, the temporal and spatial coverage may be insufficient to reliably estimate local and regional contributions to the total particle mass. Also, when there are few monitors, missing data may bias the background estimate since each observation may represent a large spatial and temporal domain.

2.2 Regional Component

Table 9 lists the statistics of the annual average regional component in St. Louis computed using the following methods: (1) upwind data from the two most isolated monitor sites (either site 9 or 10), denoted up-2; (2) upwind data from four monitoring sites (sites 6, 8, 9, 10), called up-4; (3) the lowest concentration among the ten monitors at each sampling period, low-1; and (4) the second and third lowest concentrations among the monitors, low-2 and low-3. Statistics of the two most isolated monitors are also shown. The estimates in the table are based on identical time periods. We used data only when at least 8 sites, including upwind sites, experienced concentrations

larger or equal to $3 \mu\text{g}/\text{m}^3$. These constraints eliminate much of the data, leaving only about 250 observations.

TABLE 9. ANNUAL AVERAGE REGIONAL COMPONENT IN ST. LOUIS
(std.=standard deviation; $\mu\text{g}/\text{m}^3$).

	-----fine fraction-----				-----coarse fraction-----			
	average	minimum	maximum	std.	average	minimum	maximum	std.
upwind method								
up-2	13.7	3.1	50.1	7.2	15.6	3.0	57.3	10.2
up-4	14.8	4.2	44.9	7.2	15.0	3.0	57.3	9.2
lowest method								
low-1	11.4	3.0	49.0	7.4	10.4	3.0	37.6	6.2
low-2	13.6	3.2	57.9	7.9	13.3	3.3	38.1	7.3
low-3	15.3	3.6	60.6	8.6	15.4	4.1	45.3	8.0
regional monitor								
site 9	15.9	3.0	63.9	9.8	16.2	3.0	63.0	11.9
site 10	14.0	3.0	49.0	7.8	15.1	3.1	54.1	8.8

The estimates of the regional component are similar in the two size fractions and range from 10 to $16 \mu\text{g}/\text{m}^3$. The smallest regional components are obtained using the lowest monitor. Estimates based on 4 upwind monitors are slightly greater those of 2 monitors. Concentrations at the two isolated sites are still larger. Coarse fraction estimates are more variable than fine fraction levels and may indicate local contributions at rural sites, perhaps due to agricultural activity. The $4\text{--}6 \mu\text{g}/\text{m}^3$ difference between the low-1 estimate and levels at sites 9 and 10 suggest that the latter may have been affected by local sources. Counterintuitively, the regional monitors do not necessarily show the lowest concentration.

In Table 10, the regional component is given as a function of season. Table 10 is based on a larger number of observations than

Table 9, as simultaneous observations are not required for each estimate. (As before, periods with less than 80% of valid observations are excluded.) Fine fraction regional levels in St. Louis are highest in summer; coarse fraction levels are highest in summer and fall. The various estimates maintained the rankings of the annual level, e.g., estimates based on the second lowest concentrations are about $2-4 \mu\text{g}/\text{m}^3$ higher than those based on the lowest.

TABLE 10. ANNUAL AND SEASONAL REGIONAL COMPONENT IN ST. LOUIS
($\mu\text{g}/\text{m}^3$).

	-----fine fraction-----					-----coarse fraction-----				
	annual	wint	sprg	sumr	fall	annual	wint	sprg	sumr	fall
upwind method										
up-2	14.4	11.6	13.2	24.3	13.0	15.4	11.6	15.4	20.7	18.0
up-4	15.9	13.0	14.4	24.1	14.7	15.5	11.9	15.2	21.4	16.8
lowest method										
low-1	12.3	8.7	10.8	20.3	11.6	11.0	7.9	11.2	13.9	13.3
low-2	14.8	10.9	13.1	24.0	14.1	14.1	10.3	14.1	18.2	18.4
low-3	16.6	12.4	14.8	26.1	15.8	16.7	12.1	16.0	23.5	20.9
no. obs.	424	126	161	84	47	398	101	158	69	47

Linear correlation coefficients between the background estimates are shown in Table 11. Fine fraction correlations range from 0.83 to 0.98; coarse fraction correlations are lower, ranging from 0.68 to 0.82. Upwind and lowest background estimates have the lowest correlation.

TABLE 11. CORRELATION MATRIX OF REGIONAL COMPONENTS IN ST. LOUIS

	-----fine fraction-----						-----coarse fraction-----				
	up-2	up-4	low-1	low-2	low-3		up-2	up-4	low-1	low-2	low-3
up-2	1.000						1.000				
up-4	0.902	1.000					0.820	1.000			
low-1	0.892	0.833	1.000				0.695	0.683	1.000		
low-2	0.913	0.878	0.960	1.000			0.763	0.769	0.901	1.000	
low-3	0.900	0.871	0.952	0.985	1.000		0.783	0.777	0.826	0.929	1.000

Regional contributions in Philadelphia are developed and evaluated using a similar analysis as in St. Louis, using the lowest, 2nd and 3rd lowest concentrations in the network, as well as the most isolated monitoring site (Clarksboro). Valid observations ($>3 \mu\text{g}/\text{m}^3$) are required from five of six sites, which reduces the number of observations in this comparison from the original 62 to 52. Statistics of the regional estimates are shown in Table 12. In Philadelphia, the differences between concentrations at the regional monitor and the low-1 estimate are smaller than in St. Louis.

TABLE 12. MONTHLY AVERAGE REGIONAL COMPONENTS IN PHILADELPHIA (std.=standard deviation; $\mu\text{g}/\text{m}^3$).

-----fine fraction-----					-----coarse fraction-----				
	average	minimum	maximum	std.		average	minimum	maximum	std.
lowest method									
low-1	24.8	9.1	55.8	10.9	8.5	3.6	15.6	2.6	
low-2	27.7	9.4	63.1	11.8	11.0	5.0	18.7	2.9	
low-3	29.9	10.6	64.6	11.8	12.9	6.3	21.0	3.4	
regional monitor									
Clksboro	28.2	9.1	60.3	12.7	9.6	3.6	19.4	3.3	

Table 13 shows linear correlation coefficients computed between the regional estimates. As in St. Louis, fine fraction estimates have

high correlation (0.91-0.99); coarse fraction estimates have somewhat lower correlation (0.63-0.88).

TABLE 13. CORRELATION MATRIX OF REGIONAL COMPONENTS IN PHILADELPHIA

	-----fine fraction-----					----coarse fraction-----			
	low-1	low-2	low-3	Clks.		low-1	low-2	low-3	Clks.
low-1	1.000					1.000			
low-2	0.968	1.000				0.774	1.000		
low-3	0.957	0.989	1.000			0.725	0.879	1.000	
Clks.	0.927	0.920	0.913	1.000		0.817	0.674	0.625	1.000

In summary, St. Louis and Philadelphia results are quite similar. Depending on whether upwind or lowest concentrations are used, the regional estimates vary by about 25% in the fine fraction and by about 35% in the coarse fraction. All methods have high correlation, especially in the fine fraction. Upwind estimates are comparable to the second or third lowest concentrations. The lowest concentration in the network at each time has a different distribution than other estimates.

The evaluation highlights the limitations in estimating regional contributions from limited observations. Contributions from local sources may bias estimates of the regional component. Apparently even isolated sites may be affected by local sources under some circumstances. Consequently, the so-called upwind site may not always receive the lowest concentration. In St. Louis, upwind measures are often 20 to 30% higher than the lowest. Although recognizing that the lowest concentration in the network also may be most prone to measurement errors (because it is the lowest), we use the lowest concentration in the network for a given averaging time as the

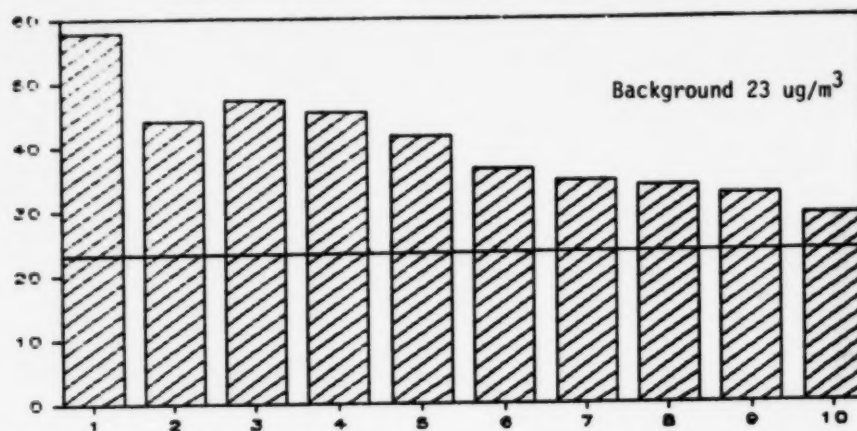
"background," or regional component. This is a conservative estimate, and uses all the available information from the relatively large number of monitors that were deployed in St. Louis and Philadelphia.

2.3 Local Contributions

The annual average concentrations at the 10 St. Louis sites of the PM-15, fine and coarse fractions are plotted in Figure 9. The background share averages 57.5% of the PM-15 at the 10 sites. The fine fraction background is 60%; the coarse fraction background is 55%. The ratio of average concentrations at the central industrial site (No. 1) to the most outlying site (No. 10) is only about 2 for PM-15, 1.75 for fine fraction, and 2.3 for coarse. There are two significant conclusions to be drawn from Figure 9. Concentrations at rural sites are due almost entirely to background particles and therefore receive little contribution from the metropolitan St. Louis sources. Equally important, the background concentration is a significant fraction of the total concentration at each site, even for the central city sites.

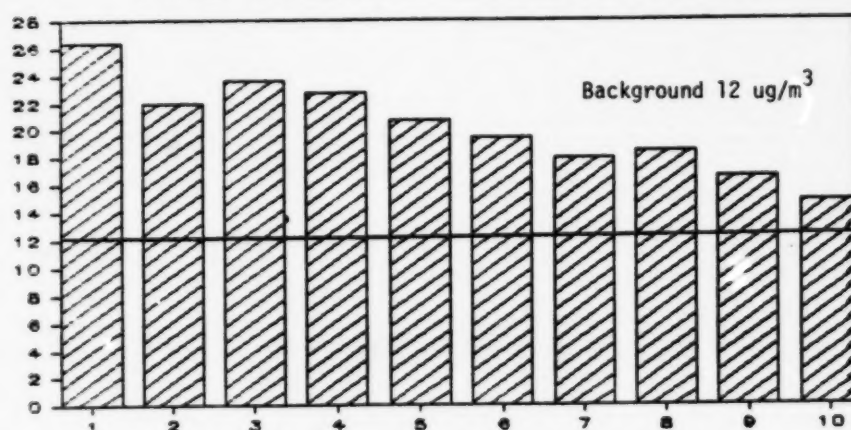
To elaborate this point further, in Figure 10 we plot the daily concentrations at the 10 sites for all days for which data are available in 1976 versus the background concentrations on that day. For any background concentration, the vertical spread of the points indicates the range of the 24-hourly concentrations at the individual sites. The lower envelope line projects the background concentration onto the ordinate. In the left half of the figure, where concentrations are low, the spread between individual sites can be

Total PM-15 Concentration

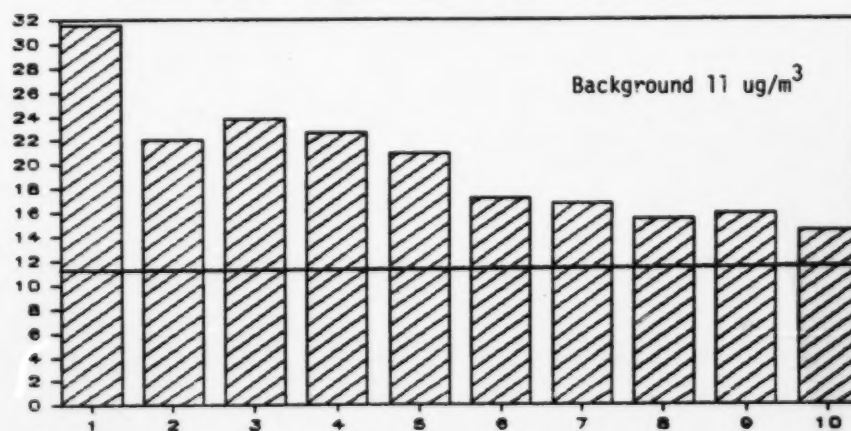


CONCENTRATION (ug/m³)

Fine Fraction Concentration



Coarse Fraction Concentration



SITE NUMBER

Figure 9. Annual (1976) average concentrations at the 10 sites in St. Louis. Upper: total PM-15; middle: fine fraction; lower: coarse. Background bar: annual average lowest.

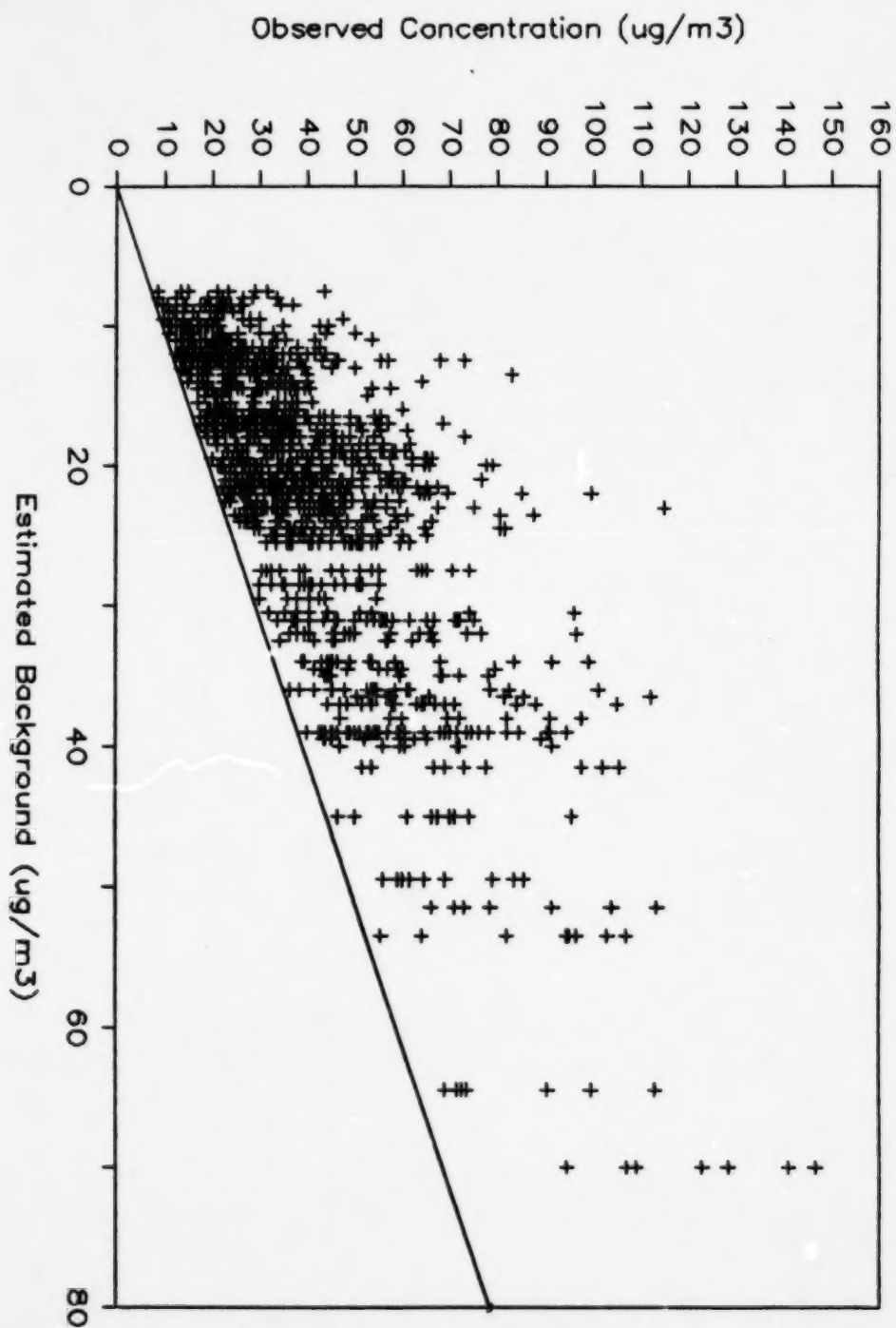


Figure 10. 24-hour PM-15 concentrations at the 10 sites in St. Louis in 1976. Lower envelope line-estimated backgrounds. Vertical spread indicates concentration range at the 10 sites.

several times the background concentration. However, on high pollution days (right half of figure), the ratio of the highest to lowest concentrations rarely exceeds 2. The interesting conclusion is that on low pollution days local sources may contribute relatively more to the total concentrations. On high pollution days (when standards are likely to be exceeded), local impacts become less pronounced and most particles seem to come from outside the network.

The monthly average concentrations at the 6 Philadelphia sites of total, fine, and coarse fractions are plotted in Figure 11. Clarksboro was the most rural of the sites, probably least impacted by local sources. Fireboat was deployed near ongoing construction activity; this site gave peculiar results. Site-averaged concentrations are computed for 5 sites only, excluding Fireboat. The background share of the average PM-10 concentration is 77%. The fine fraction background is 83%; the coarse 64%. The ratio of concentrations at the center city site Broad Street to that at Clarksboro is less than 1.2 for total mass and fine fraction, and 1.6 for the coarse fraction. Thus, in Philadelphia the background share is even larger than in St. Louis, and the relative difference between city center and outskirts is smaller. These differences between Philadelphia and St. Louis may be due in part to the smaller size cutoff of the coarse fraction inlet and to the difference between summer and annual averages.

The daily concentrations are plotted in Figure 12, in which the letter symbols stand for the 6 sites. The envelope line equals the background concentration; the spread indicates the range of concentrations at the sites. Excluding the Fireboat site (F), we see

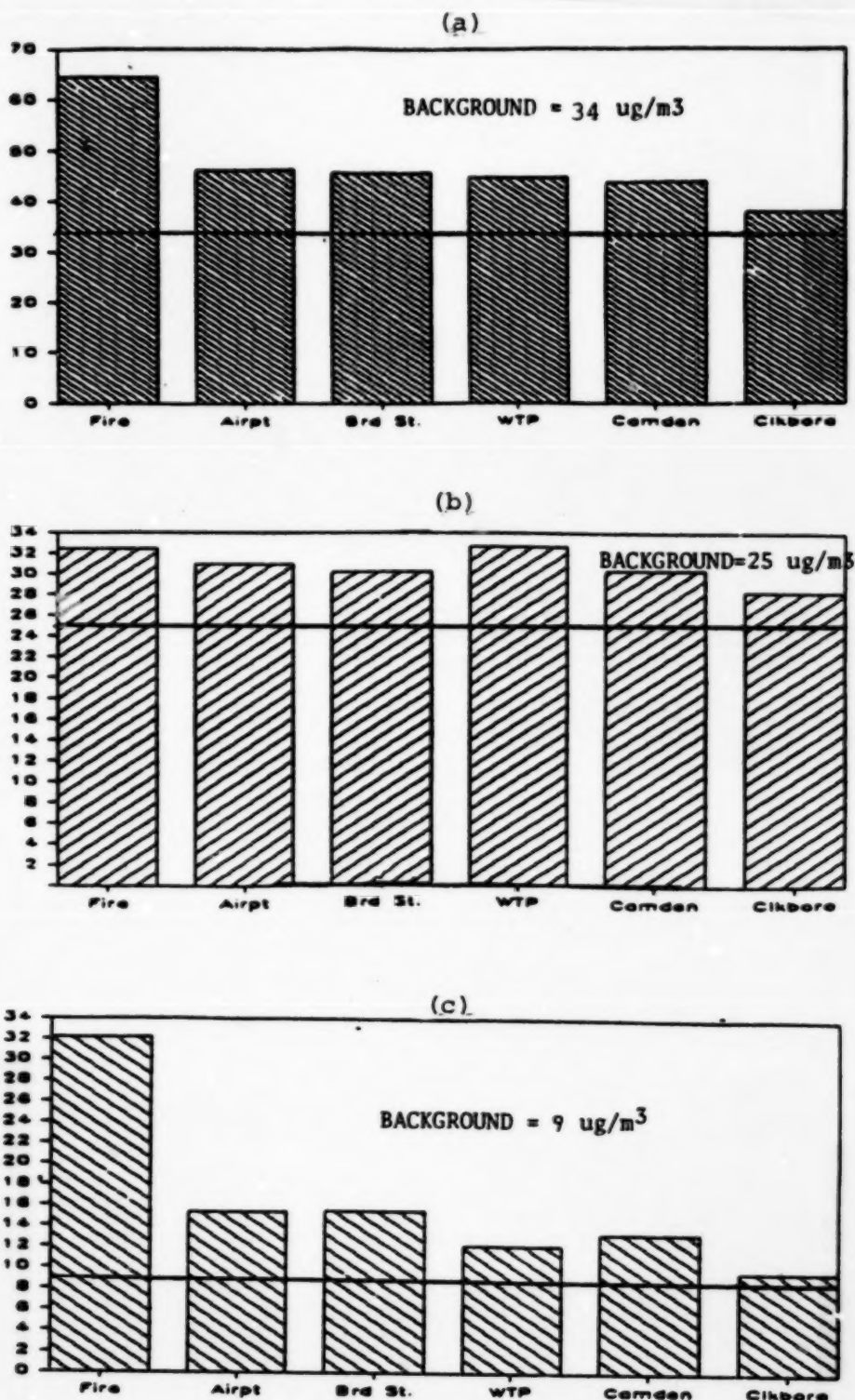


Figure 11. Monthly average concentrations at the 6 sites in Philadelphia. Upper: total PM-10; middle: fine fraction; lower: coarse. Background bar monthly average lowest.

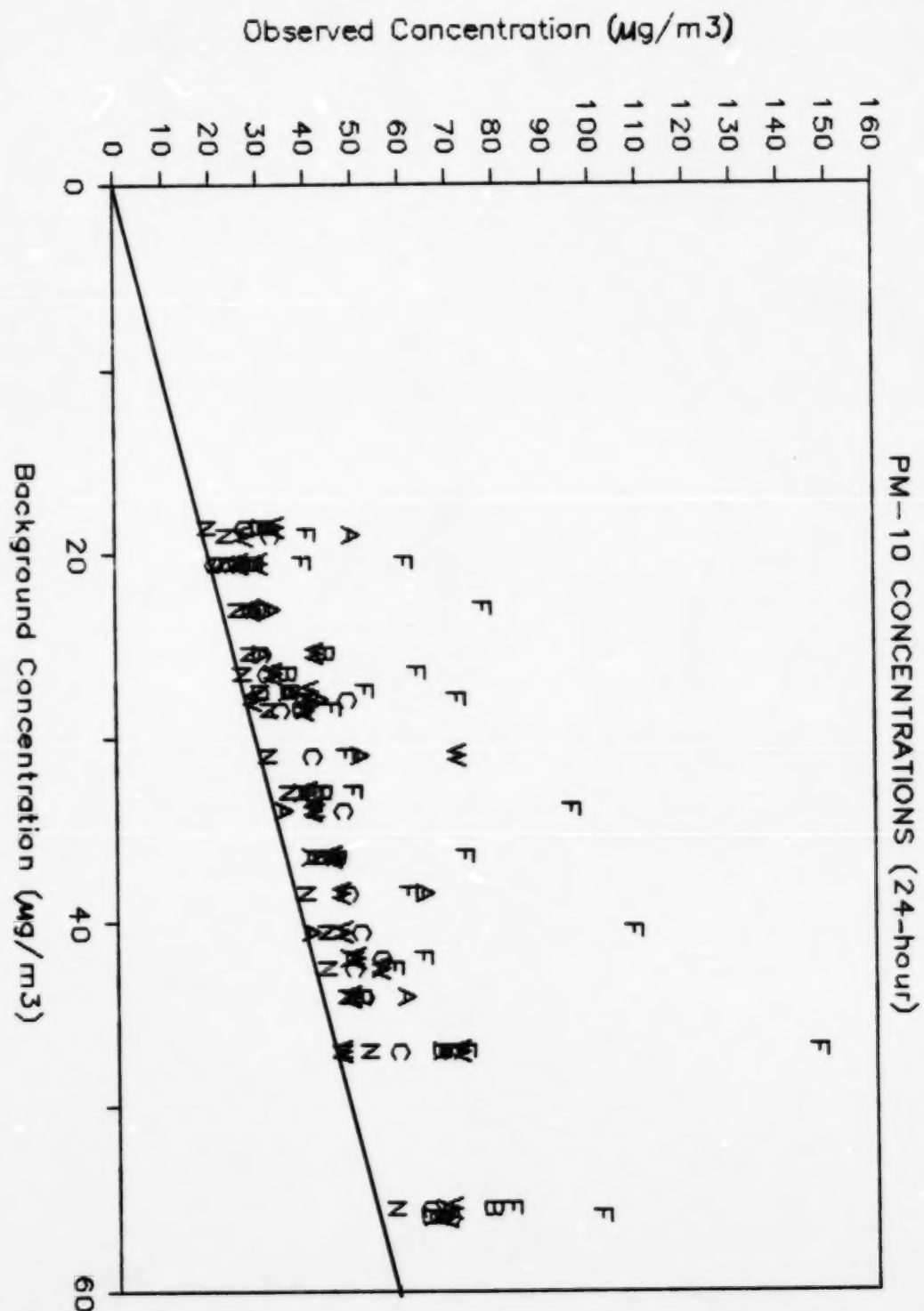


Figure 12. 24-hour PM-10 concentrations at the 6 sites in Philadelphia. Lower envelope line-estimated background. Vertical spread indicates concentration range at the 6 sites. Note exceptional high values at Fireboat (F).

that the range is usually less than twofold. As in St. Louis, the range is greater at lower overall concentrations. This again indicates that the proportionate contribution of local sources is less at high concentrations when exceedances might occur.

In summary, the regional component composed well over half of the average fine fraction levels at most monitors in both cities, and about half of the coarse fraction concentrations. The background fraction is relatively constant; thus, local and regional levels appear to change together. The correlation of local and regional concentrations suggests that meteorological factors are the dominant influences on both components.

2.4 Regional and Local Levels of SO_4

Because SO_4 is the principal constituent of fine fraction concentrations, it is interesting to estimate its regional and local components. This is shown in Tables 14 and 15. (The measured elemental S is multiplied by 3.) (Coarse fraction SO_4 concentrations are negligible, approximately $0.2 \mu\text{g}/\text{m}^3$.)

In summer, regional SO_4 concentrations in St. Louis and Philadelphia are similar, 8.2 and $7.5 \mu\text{g}/\text{m}^3$, respectively. In summer, local sources contribute an average of 4.2 and $2.6 \mu\text{g}/\text{m}^3$ in the two cities. In St. Louis, rural monitors have slightly lower SO_4 levels than urban monitors. In Philadelphia, however, the most isolated monitor (Clarksboro) has slightly higher SO_4 levels than three of the urban sites.

TABLE 14. ESTIMATED REGIONAL SO₄ LEVELS
($\mu\text{g}/\text{m}^3$)

	-----St. Louis-----				--Philadelphia--	
	---annual---		---summer---		---summer---	
	avg.	max.	avg.	max.	avg.	max.
low-1	5.1	25.1	8.2	25.1	7.5	25.6
low-2	6.1	28.3	9.8	28.4	9.2	27.1
low-3	6.5	29.9	10.4	29.8	9.8	29.4

TABLE 15. ESTIMATED LOCAL SO₄ CONTRIBUTIONS
($\mu\text{g}/\text{m}^3$).

	-----St. Louis sites-----										
	1	2	3	4	5	6	7	8	9	10	avg.
	low-1										
annual	3.4	3.1	3.7	3.3	2.7	2.8	2.0	2.0	2.0	1.6	2.7
summer	5.7	4.8	4.8	4.6	4.9	3.9	3.5	3.2	2.9	na	4.2

-----Philadelphia sites-----							
Air	Camden	Clks.	Broad	Fire	WTP	avg.	low-1
2.1	3.4	2.9	2.5	1.5	3.3	2.6	7.5

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SECTION 3

APPLICATION AND EVALUATION OF DISPERSION MODELING

3.1 Introduction

This section describes the application and evaluation of dispersion modeling based upon data from St. Louis and Philadelphia. The Particle Episodic Model (Rao and Stevens, 1985) was described and evaluated in the First Annual Report of this Cooperative Agreement (Batterman et al., 1985). Here we apply a long-term version of PEM to apportion and predict particle concentrations in St. Louis and Philadelphia. The long-term (monthly) version is based on the joint probability functions of the meteorological variables: stability class, wind direction, speed, and mixing height. The standard plume rise formula and McElroy-Pooler dispersion coefficients are used. Details of this version of PEM are presented in Batterman (1986). In the St. Louis and Philadelphia model evaluation, only the local contributions are modeled. The observed local component is obtained by subtracting the regional component as described in the preceding section.

3.2 Dispersion Modeling in St. Louis

Emission Inventory. Emission rates for St. Louis were obtained from Brock (1984) for area sources, and from the RAPS inventory for point sources. Size fractionated particle emission rates in St. Louis were derived from TSP estimates using different size classifications in a post hoc fashion. An effective height of 30 m is assumed for SO_x emission sources, and 10 m for particle emission sources. Area

sources are combined into 12 X 12 grid cells of 5 km² each. Area sources include mobile sources (automobile) emissions. In view of the poor modeling results, the St. Louis estimated PM-15 emission inventory is deemed less accurate than the estimated Philadelphia PM-10 inventory.

Meteorological Observations. Meteorological observations were measured at 25 widely dispersed sites; modeling uses the network average, which should minimize local influences.

Transformation Rates. For SO₂ to SO₄ transformation, we used a rate of 5% per hour in daytime and 2% per hour in nighttime (National Research Council, 1983). Settling and deposition rates for all modeled particles were assumed to be zero. A previous sensitivity analysis (Batterman et al., 1985) showed that incorporating deposition and settling processes in urban models will produce only minor changes in predicted concentrations on the urban scale, especially for the deposition and settling velocities appropriate for inhalable particles.

Particle Measurements. Continuous observations from a one-month summer period in 1976 are used in order to enable a comparison with the Philadelphia study. Typically, summer particle concentrations are higher due to higher production of secondary pollutants and slower wind speeds. The St. Louis monitoring sites were widely dispersed and provided excellent coverage of the region.

Model Predictions and Evaluation. The estimated monthly-average particle concentrations are given in Table 16. Contributions from area and point sources are listed separately. On average, area sources contribute the bulk of particle predictions. The highest point source contribution of $4.2 \mu\text{g}/\text{m}^3$ (at site 2) represents less than 5% of the total prediction. Area source contributions in each particle size range are similar. Point sources contribute most of the SO_4 .

TABLE 16. MONTHLY AVERAGE PREDICTIONS IN ST. LOUIS
($\mu\text{g}/\text{m}^3$).

	-----site number-----										average
	1	2	3	4	5	6	7	8	9	10	10-site
particles (primary)											
area											
<3 μm	22.5	37.4	38.3	20.5	28.7	14.7	14.1	22.4	4.7	2.2	18.7
3-7 μm	20.8	26.0	30.1	22.4	22.0	23.0	22.1	25.9	5.7	3.1	18.3
>7 μm	15.2	20.5	23.3	16.2	17.5	15.9	15.4	19.6	4.1	2.2	13.6
point	1.3	4.2	0.8	1.2	1.5	0.5	0.4	0.4	0.5	0.1	1.0
total	59.8	88.1	92.5	60.3	69.7	54.0	51.9	68.2	15.0	7.6	51.6
SO_4 (secondary)											
area	0.30	0.47	0.39	0.20	0.29	0.17	0.32	0.20	0.09	0.21	0.26
point	0.50	0.65	0.60	0.32	0.45	0.30	0.62	0.42	0.15	0.33	0.43
total	0.80	1.11	0.99	0.51	0.74	0.47	0.93	0.62	0.24	0.53	0.69

Table 16 also shows secondary SO_4 predictions (primary SO_4 emissions were not available). Littman et al. (1977) estimated that about 2% of the sulfur may be emitted as primary SO_4 . Accordingly, the modeled primary SO_4 concentrations are only slightly smaller than the modeled secondary SO_4 concentrations, 0.6 versus $0.7 \mu\text{g}/\text{m}^3$, respectively. The highest monthly average SO_4 prediction occurs at site 2: $3 \mu\text{g}/\text{m}^3$ (1.1 secondary + 1.9

$\mu\text{g}/\text{m}^3$ primary).

The estimated contributions of the top three area and point sources at the receptors are shown in Table 17. The table lists the average contributions to the 10 receptors as well as to those with the highest predictions. One or two sources at each site provide most of the local increment. For example, a single area source cell at each receptor--usually the "host" cell containing the receptor--contributes an average of $11 \mu\text{g}/\text{m}^3$ of the total fine fraction prediction of $19 \mu\text{g}/\text{m}^3$ due to area sources. At receptors with the highest concentrations, host cells provide about half of the mass. For example, of $38 \mu\text{g}/\text{m}^3$ predicted at the receptor with the highest fine fraction concentration (site 2), $22 \mu\text{g}/\text{m}^3$ is provided by the host cell. These results indicate that predictions are extremely sensitive to emissions of the host cell. Sources near receptors may be inaccurately modeled due to the assumption of uniform emissions throughout the relatively large 5 km^2 cells.

TABLE 17. MAJOR CONTRIBUTORS TO PREDICTED CONCENTRATIONS IN ST. LOUIS
($\mu\text{g}/\text{m}^3$).

	-----particles-----					
	<3 μm dia.		3-7 μm dia.		>7 μm dia.	
	aver	max	aver	max	aver	max
	area sources					
highest	10.8	21.9	7.4	14.3	5.9	11.4
2nd high	1.5	3.8	1.1	2.4	0.8	2.1
3rd high	0.9	1.6	0.7	1.2	0.5	0.8
TOTAL	18.7	38.3	18.3	30.1	13.6	23.3
	point sources					
highest	0.6	3.3	na	na	na	na
2nd high	0.2	0.4	na	na	na	na
3rd high	0.1	0.2	na	na	na	na
TOTAL	1.0	4.2	na	na	na	na

The largest particle contributors at several sites include a cement

company (Missouri Portland), steel works (Granite City) and several industrial sources (PVO International, Monsanto, Olin, Clark Oil). For cement and steel industries, PM-15 emissions derived from TSP emissions may be overestimated, since a large fraction of particles may be greater than 10 μm in diameter.

The model is evaluated by comparing predictions and observations. Scatterplots of monthly average observed and predicted concentrations are shown in Figure 13. Only the local component of ambient concentrations is shown, that is, the background is subtracted from observations. A scatterplot for observed and predicted SO_2 concentrations is also included, although SO_2 modeling was not part of this Cooperative Agreement. Observed and predicted SO_2 levels match closely, both in level and spatial distribution. SO_4 predictions have the correct spatial pattern, but are underpredicted, possibly because primary SO_4 emissions and/or transformation rates are underestimated. Particle concentrations are greatly overpredicted, especially in the coarse fraction. In addition, particle predictions do not reflect the observed spatial distribution. For example, high coarse fraction concentrations--comparable to those at the urban sites--are predicted at outlying receptors, e.g., sites 7 and 8. These errors may result from overestimating background, however, this would not alter the predicted spatial distribution. Errors in the emission inventory would affect both the level and distribution of predictions. Such errors seem likely considering the relatively crude derivation of size-fractioned particle emission rates in St. Louis.

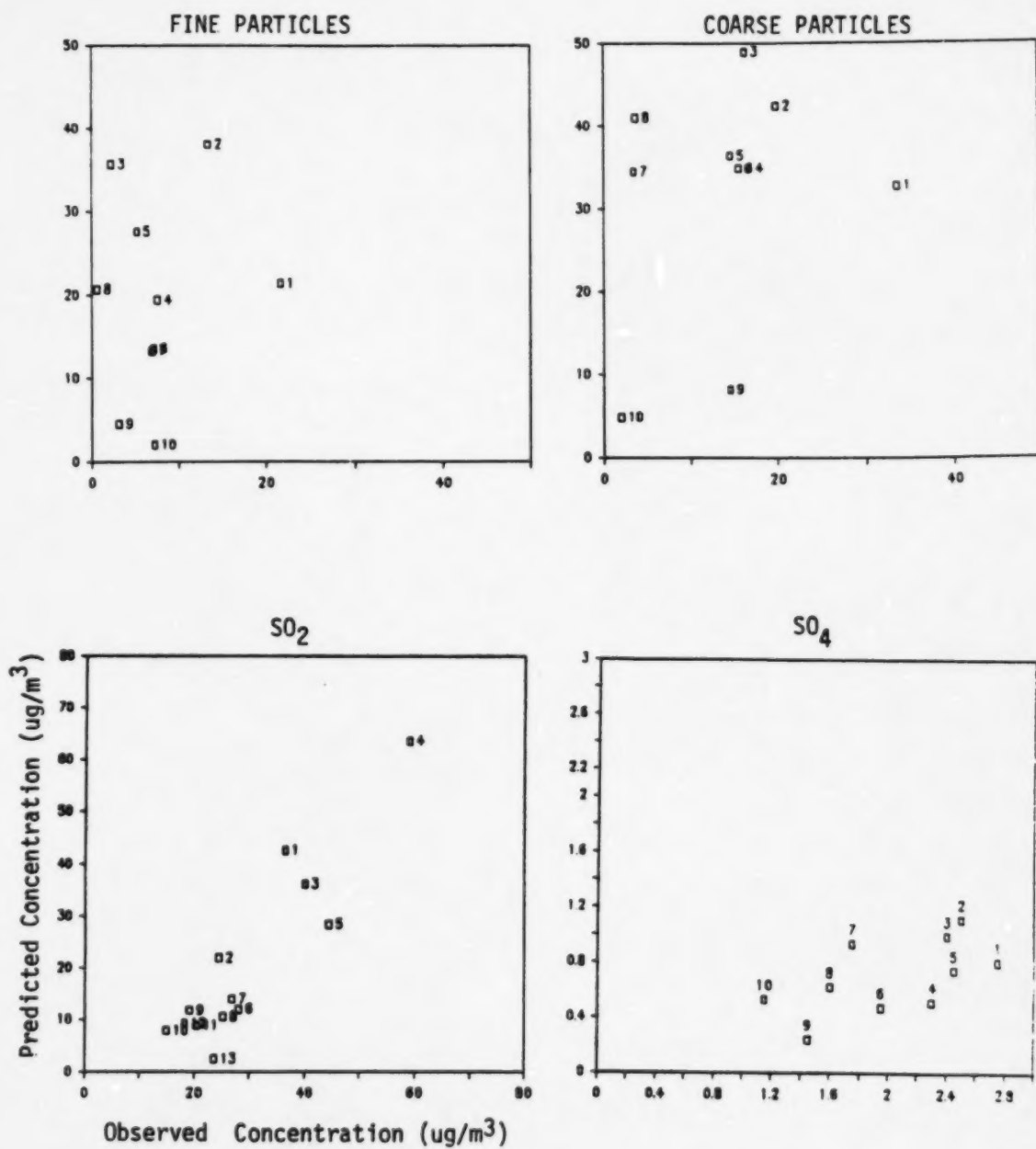


Figure 13. Scatterplots of monthly average observed versus predicted local concentrations in St. Louis. (number indicates receptor site).

The derived linear correlation coefficients for short-term modeling are shown in Table 18. For SO_2 , hourly averages are used; for particles, 12-hour averages are used, corresponding to the available observations. Correlation coefficients are quite low; the highest ones only reaching 0.4 - 0.5 at a few sites.

TABLE 18. SHORT-TERM MODELING CORRELATION COEFFICIENTS AT ST. LOUIS SITES

	-----site number-----													
	1	2	3	4	5	6	7	8	9	10	11	12	13	average
SO_2	0.14	0.45	0.43	0.16	0.06	0.02	-0.0	-0.04	0.36	0.50	-.15	0.01	0.10	0.16
fine	-.13	0.06	0.42	0.29	0.48	-0.2	0.28	0.12	-.04	0.54	na	na	na	0.18
coarse	0.48	0.44	0.21	0.37	-.04	-0.1	0.24	-.07	0.41	na	na	na	na	0.24

Table 19 lists particle levels stratified by various meteorological factors. Concentrations are listed only for those 12-hour periods that experienced 4 or more hours of very unstable (A and B) or very stable (E and F) conditions. High winds tend to reduce fine fraction observations and predictions. Stable conditions cause slight decreases of observed levels, but greatly increase predictions. Similar results are obtained for coarse particles. Particle concentrations are also sensitive to rainfall. Again, it is seen that predictions/observations match quite poorly for the fine fraction; however, better agreement is obtained in the coarse fraction.

3.3 Dispersion Modeling in Philadelphia

Emission Inventory. In Philadelphia, emissions from area and point sources for fine ($<2.5 \mu\text{m}$ dia.) and coarse ($2.5\text{--}10 \mu\text{m}$) size fractions were obtained from Toothman (1984). Fine fraction emissions are roughly twice the coarse fraction emissions in each source category, i.e., major, minor, mobile, and area categories. Unlike St. Louis, in Philadelphia separate day and night emission

TABLE 19. MONTHLY AVERAGE CONCENTRATIONS IN ST. LOUIS, STRATIFIED BY METEOROLOGICAL AND TEMPORAL FACTORS ($\mu\text{g}/\text{m}^3$).

	-----observed-----			--predicted local--		--sample size--		
	local	region	total	area	point	total	meteor	observ
fine fraction								
average	15.8	17.7	33.5	18.6	1.0	19.6	59	306
wind > 3 m/s	9.4	20.2	29.6	12.0	0.9	12.9	29	186
mix > 1000 m	14.7	19.7	34.4	13.2	0.9	14.1	20	182
rain > .02"	14.9	12.8	27.8	17.5	1.2	18.7	14	93
stab A+B>4hr	27.8	13.2	41.0	19.5	0.8	20.3	9	79
stab E+F>4hr	19.9	23.7	43.6	29.8	0.9	30.8	13	101
coarse fraction								
average	14.1	13.0	27.1	31.8	na	31.8	59	307
wind > 3 m/s	13.2	12.4	25.6	20.8	na	20.8	29	186
mix > 1000 m	15.2	11.1	26.2	22.8	na	22.8	20	182
rain > .02"	7.8	12.2	20.0	29.5	na	29.5	14	93
stab A+B>4hr	21.7	12.7	34.5	33.5	na	33.5	9	79
stab E+F>4hr	18.1	17.3	35.3	51.2	na	51.2	13	101

rates are available.

Meteorological Observations. Surface meteorological data were collected at the International Airport (in South Philadelphia). Surface observations were also obtained for the closest meteorological site, located in Norristown about 15 miles north. A comparison of these data indicates that wind directions in Norristown are sometimes 60 or more degrees different than at the Airport. However, on the average, directions are fairly similar at both sites.

Particle Measurements. For Philadelphia, 12-hour particle measurements at 6 sites during the period 15 July to 14 August, 1982 are available. Unfortunately, 6 receptors may not adequately characterize the spatial distribution of particles in as large and diverse a city as Philadelphia.

Model Predictions and Evaluation. Modeling results are given in Table 20. Monthly average concentrations are estimated for the 6 particle monitoring sites. Estimates of SO_2 concentrations at the 6 sites are also given for completeness. Area sources contribute about 80% of particle predictions. Only at the rural Clarksboro site are particle contributions from area and point sources similar. Area source predictions are composed of comparable minor point and area source contributions; mobile source contributions are somewhat smaller. Area sources provide about half of the primary SO_4 . On average, primary SO_4 constitutes 57% of the total predicted SO_4 level of $2.5 \mu\text{g}/\text{m}^3$. The Broad Street site has the highest SO_4 concentration of $3 \mu\text{g}/\text{m}^3$. However, SO_4 predictions are similar at all sites. As in St. Louis, secondary SO_4 predictions are slightly greater than primary SO_4 predictions.

The contributions of the largest three area and point sources averaged at the 6 receptors and the contributions at receptors with the highest concentrations are shown in Table 21. As in St. Louis, the highest area source contributor is either the host cell or an adjacent cell. Contributions from other cells are usually much smaller. The largest contributors account for 42% of the total concentration predicted from all area sources. In Philadelphia, host cells provide a larger fraction at receptors with high concentrations than in St. Louis, accounting for 62% of particles and about half of the SO_4 at the Broad Street receptor. Point sources provide an average of 22% of the particles from all sources. In no case is the largest point source contribution more than one third of the total.

A single power plant (Eddystone) is the largest point source contributor

TABLE 20. MONTHLY AVERAGE PREDICTIONS IN PHILADELPHIA
($\mu\text{g}/\text{m}^3$).

		-----site-----						-----average-----
		Apt	Cam	Clk	Brd	Fbt	WTP	6-site
fine particles (primary)	area	5.6	7.6	1.9	13.8	7.1	7.2	7.2
	point	1.0	1.7	1.4	1.3	1.5	1.3	1.4
	total	6.7	9.3	3.3	15.1	8.6	8.4	8.6
coarse particles (primary)	area	3.4	4.8	1.2	8.0	3.8	4.6	4.3
	point	0.6	1.3	0.5	0.7	1.0	0.6	0.8
	total	3.9	6.1	1.8	8.7	4.8	5.2	5.1
SO ₂	area	8.9	14.3	9.3	23.3	22.0	11.2	14.8
	point	11.0	22.5	21.7	27.2	20.4	16.7	19.9
	total	19.9	36.8	31.0	50.5	42.4	27.9	34.8
SO ₄ (primary)	area	0.38	0.64	0.32	1.04	0.97	0.47	0.64
	point	0.29	0.78	0.83	0.79	0.61	0.45	0.63
	total	0.67	1.42	1.15	1.83	1.58	0.92	1.26
SO ₄ (secondary)	area	0.39	0.44	0.38	0.45	0.45	0.36	0.41
	point	0.53	0.75	0.74	0.69	0.60	0.65	0.66
	total	0.92	1.19	1.10	1.14	1.07	1.01	1.07

TABLE 21. MAJOR CONTRIBUTORS TO PREDICTED CONCENTRATIONS IN PHILADELPHIA
($\mu\text{g}/\text{m}^3$).

	-----particles-----				---SO ₂ ---	
	<3 μm dia.		3-10 μm dia.		aver	max
	aver	max	aver	max		
area sources						
highest	3.1	9.0	2.1	5.3	7.2	14.6
2nd high	0.5	1.0	0.3	0.4	1.7	2.5
3rd high	0.3	0.6	0.2	0.3	1.0	1.6
TOTAL	7.5	13.8	4.5	8.0	17.9	23.3
point sources						
highest	0.4	0.7	0.2	0.3	4.9	8.9
2nd high	0.2	0.4	0.1	0.2	2.8	5.6
3rd high	0.1	0.2	0.1	0.1	1.6	4.2
TOTAL	1.4	1.7	0.7	1.3	21.9	27.2

of fine particles at all receptors. Other important contributors include a second coal power plant (Cromby), an oil refinery (Mobil), and several industrial facilities (J.D. Morrissey at Airport, Frostie and Predco at Camden, EC Incinerator and Franklin Smelter at Fireboat, Glasgow at Belmont, WTP). For coarse particles, the important point sources include a power plant (Eddystone), incinerators (EC and NW), oil refineries (Mobil, Getty), a chemical plant (Harshaw) and several other sources.

Scatterplots of monthly average observations and predictions are shown in Figure 14. Note that observed concentrations have subtracted the regional component. As in St. Louis, the bulk of fine particles and SO_4 concentrations is of regional origin. Fine fraction concentrations at the Broad Street receptor are overpredicted. Coarse fraction levels at the Fireboat are underpredicted as expected, since strong nearby sources are not included in the inventory. Coarse fraction concentrations are also underpredicted at the Airport site. The spatial pattern at the remaining sites is correctly modeled. A scatterplot of SO_2 concentrations is also given. SO_2 was monitored at 12 sites; therefore, 12 data points appear in the scatterplot.

Estimated linear correlation for short-term pollutant levels are listed in Table 22. They range from -0.31 to 0.68. SO_2 has the highest

TABLE 22. LINEAR COELATION COEFFICIENCTS AT PHILADELPHIA SITES

	-----site number-----												
	Apt	Cam	Clk	Brd	Fbt	WTP	7	8	9	10	11	12	average
SO_2	0.23	0.08	0.00	0.22	0.45	0.53	0.49	0.03	0.26	0.32	0.68	0.59	0.32
fine	0.26	0.35	0.27	0.05	-0.31	0.01	na	na	na	na	na	na	0.11
coarse	0.10	0.04	-0.2	-0.07	-0.15	0.03	na	na	na	na	na	na	-0.05

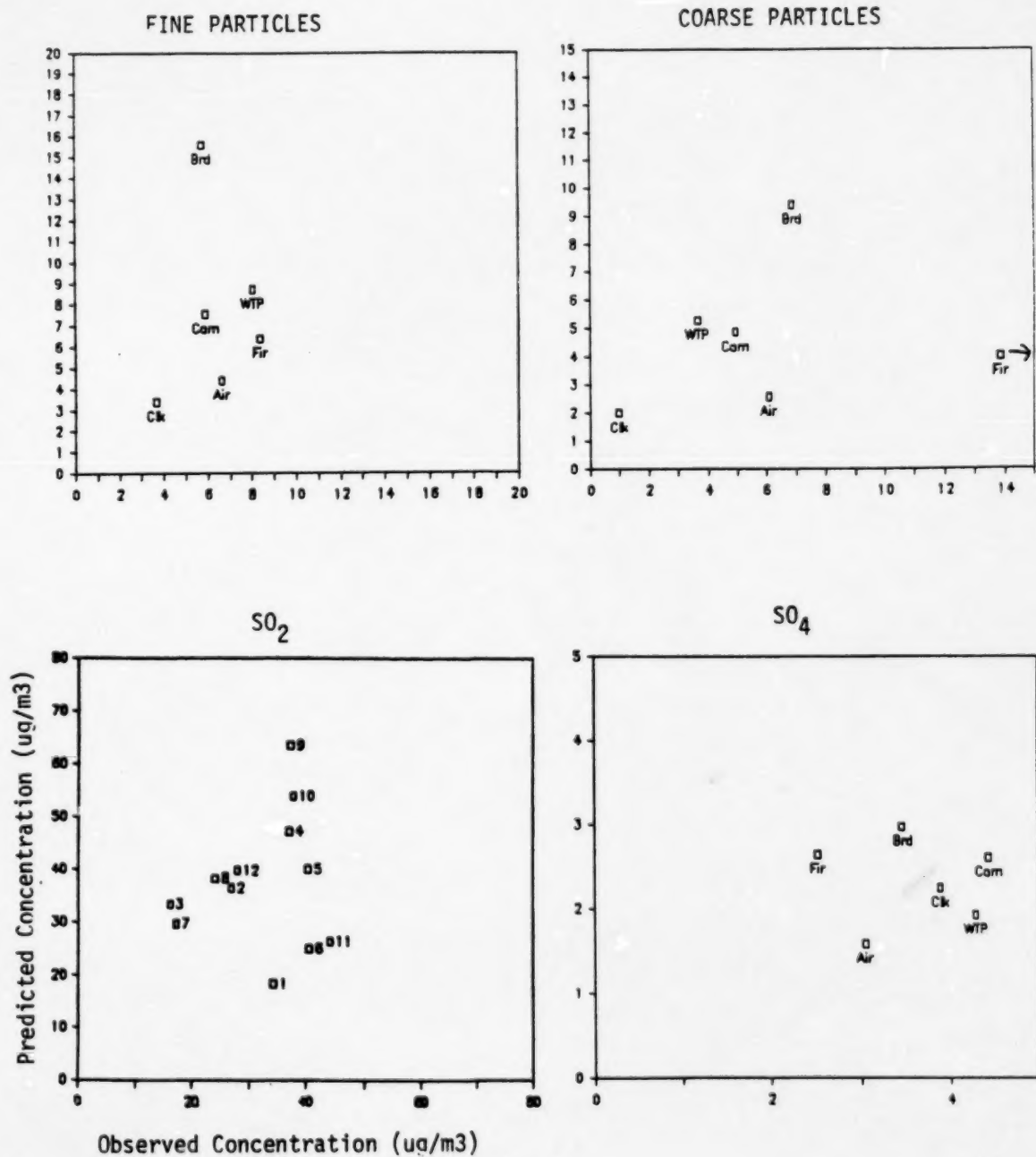


Figure 14. Observed versus predicted local concentrations in Philadelphia. (number indicates receptor site.)

correlation; coarse concentrations have essentially zero correlation. As in St. Louis, short term predictions bear little relationship to observations at most receptors.

Table 23 shows particle levels stratified by day and night, wind speed, mixing height, and concentrations in 12-hour periods that experienced 4 or more hours of very unstable (A and B) or very stable (E and F) conditions. In the fine fraction, day-time observed levels decrease with rain; however, at night, levels may increase somewhat. Predicted levels are reduced in periods of high winds. Coarse fraction observations show little change. As in St. Louis, at night under stable dispersion conditions and low winds, predictions increase. Similarly to St. Louis, the major discrepancies in the model appear to be related to the treatment of stability.

3.4 Comparison of St. Louis and Philadelphia

A comparison of St. Louis and Philadelphia emission rates is given in Table 24. Estimated Philadelphia fine fraction emissions are about twice the coarse fraction, whereas in St. Louis the coarse fraction emissions are estimated to be higher. These estimates may in part explain the observed differences of ambient particle levels in the two cities. A comparison of monthly average predictions and observations in the Philadelphia and St. Louis studies is presented in Table 25. Area sources are the primary contributors of particles. Host cells, the area source cell in which the receptor is located, account for about half of the total particle prediction. Point sources produce roughly half of the SO_2 and SO_4 . Generally, a few sources provide most of the contributions at the receptors.

In St. Louis, however, particle levels are overpredicted, especially in the coarse fraction, and predictions do not have the correct spatial distribution.

TABLE 23. PARTICLE CONCENTRATIONS IN PHILADELPHIA STRATIFIED BY
TEMPORAL AND METEOROLOGICAL FACTORS
($\mu\text{g}/\text{m}^3$)

fine fraction	-----observed-----			--predicted local--			-sample size-	
	local	region	total	area	point	total	meteo.	obser.
average	6.4	24.5	31.0	7.3	1.4	8.6	58	306
day average	5.9	25.8	31.7	4.4	0.6	5.0	29	154
night average	7.0	23.3	30.3	10.1	2.2	12.3	29	152
day u > 3.9 m/s	5.2	21.2	26.4	4.2	0.7	4.9	17	91
night u > 2.8 m/s	7.2	23.8	31.0	7.9	1.9	9.9	18	95
day mix > 1300 m	5.2	27.8	33.1	4.1	0.6	4.7	20	18
night mix > 700 m	7.6	24.5	32.1	9.2	1.8	10.9	14	74
day rain > 0.02"	3.9	20.8	24.7	4.1	0.5	4.7	7	38
night rain > 0.02"	8.2	26.4	34.5	9.4	2.0	11.4	11	55
stability = AB	5.3	24.7	30.0	3.8	0.6	4.3	15	79
stability = EF	7.3	21.3	28.6	10.8	2.6	13.4	19	101
coarse fraction								
average	7.8	8.5	16.3	4.3	0.8	5.1	58	303
day average	8.6	9.2	17.7	2.9	0.5	3.3	29	151
night average	7.0	7.9	14.9	5.8	1.1	6.9	29	152
day u > 3.9 m/s	8.1	8.3	16.3	2.7	0.5	3.2	17	91
night u > 2.8 m/s	7.6	7.7	15.2	4.7	1.0	5.7	18	95
day mix > 1300 m	9.3	9.3	18.5	2.7	0.5	3.1	20	108
night mix > 700 m	8.0	8.1	16.1	5.4	1.0	6.4	14	74
day rain > 0.02"	8.9	8.4	17.3	2.7	0.4	3.1	7	39
night rain > 0.02"	9.1	7.6	16.7	5.4	1.1	6.5	11	55
stability = AB	8.2	9.8	18.0	2.5	0.4	2.9	15	79
stability = EF	7.7	7.7	15.4	5.9	1.3	7.2	19	101

TABLE 24. COMPARISON OF PHILADELPHIA AND ST. LOUIS INVENTORIES
(emission density shown in parenthesis)

		total emissions (g/s) and emission density (g/s-km ²)							
		---fine---		---coarse---		---TSP---		---SO ₂ ---	
St. Louis									
total		2502	(0.69)	3394	(0.95)	35198	na	32245	na
urban		na	na	na	na	na	na	na	na
Philadelphia									
total		950	na	454	na	na	na	5876	na
urban		239	(0.15)	151	(0.09)	na	na	976	(0.61)

TABLE 25. COMPARISON OF AVERAGE CONCENTRATIONS IN ST. LOUIS AND
PHILADELPHIA; REGIONAL COMPONENT IN PARENTHESIS
($\mu\text{g}/\text{m}^3$).

		-----St. Louis-----		---Philadelphia---	
		predicted	observed	predicted	observed
fine particles (primary)	area	18.6		7.2	
	point	1.0	(25.5)	1.4	(23.7)
	total	19.6	8.0	8.6	7.4
coarse particles (primary)	area	31.9		4.3	
	point	na	(12.9)	0.8	(8.5)
	total	31.9	14.3	5.1	7.7
SO ₂	area	11.5		14.8	
	point	10.4	(7.1)	19.9	(4.2)
	total	21.9	26.0	34.8	32.3
SO ₄ (total)	area	0.6		1.1	
	point	0.8	(7.5)	1.3	(6.5)
	total	1.3	2.7	2.3	3.6

Most likely, the St. Louis emission inventory does not accurately reflect PM-15 emissions. In St. Louis, fine and coarse particle

emissions were derived from TSP data, which in many cases may be unrelated to PM-15 emissions but to fugitive dust. At short averaging times model predictions have low correlation (0.2-0.3) with observations. In Philadelphia, long-term predictions are in reasonable agreement with measurements. The mean levels and the spatial variation at most sites are quite well modeled.

SECTION 4

STATISTICAL MODELS FOR SOURCE APPORTIONMENT

4.1 Receptor Modeling in St. Louis

Annual average apportionments for St. Louis are estimated using the multiple linear regression method (MLR). Regressions are performed separately for the fine and coarse fractions obtained at the 10 particle monitoring sites. Elements included in the regressions are selected using the "all possible regressions" (APR) procedure (Montgomery and Peck, 1982). This procedure efficiently generates many combinations of regressors and identifies the models with the best fits. Regressions are then repeated at each site using elements which had statistically significant ($p < 0.05$) coefficients at a majority of the sites.

A summary of results is shown in Table 26. The regressions explain about 50-80% of the variance of particle concentrations, as indicated by the multiple correlation coefficient (R^2). The narrow range of S, Ca and Cu coefficients indicates that these elements are stable tracers.

In the fine fraction, Al, S, and Pb have significant coefficients at most sites. S represents SO_4 and Pb is representative of vehicular emissions. As shown later, the Al factor is related to coarse crustal sources. An average of $2.8 \mu\text{g}/\text{m}^3$ or 14% of fine fraction concentrations is unexplained by these tracers. This is the intercept of the linear regression and is listed in Table 26 as "constant."

TABLE 26. REGRESSION COEFFICIENTS AND SOURCE APPORTIONMENTS
FOR SEPARATE SIZE FRACTIONS IN ST. LOUIS

element and -source class-	-estimated -average-	coefficients- ---range---	no. of sites	average observation (ng/m ³)	apportionment concentrations (μg/m ³)	percent (%)
fine fraction						
Al (crustal)	25.2	9.9 - 25.8 ¹	8	119.4	3.01	13.3
S (sulfate)	4.9	4.0 - 5.7 ¹	10	2602.6	12.75	56.0
Pb (vehicles)	8.5	3.5 - 15.3 ²	8	461.3	3.92	17.4
Constant	2.8	1.3 - 3.8	5	na	2.80	12.4
R ² /total	0.70	0.49 - 0.82	10	20200.0	22.48	100.0
coarse fraction						
Al (crustal)	11.3	7.9 - 13.3	10	914.1	10.33	51.3
S (sulfate)	12.4	5.9 - 23.0 ³	6	284.2	3.52	14.1
Cl (roadsalt?)	3.8	2.1 - 8.1 ³	6	245.2	0.93	4.6
Ca (crustal)	2.9	2.1 - 3.8 ⁴	9	2269.9	6.58	32.7
Cu (incin?)	215.7	167.4 - 263.5 ⁴	4	7.0	1.51	7.5
R ² /total	0.68	0.63 - 0.76	10	20100.0	22.87	100.0

¹ sites 1-6 averaged 5.2; sites 7-10 averaged=4.4

² sites 1-2 averaged 15.0

³ site 5=8.1; other sites averaged=3.0

⁴ sites 3,4,7,8

In the coarse fraction, Al, S, Cl, and Ca are significant predictors at most sites, and Cu is a significant predictor at four sites. Al may represent shale, Ca limestone dominated crustal material (Dzubay, 1980); S represents sulfate, Cl may indicate winter road salting, and Cu contributions from metal industries and/or incineration. Intercept terms are not statistically significant in the coarse fraction regressions.

The average source contributions are estimated as the product of regression coefficients and elemental concentrations. Annual average concentrations across the 10 sites and average regression coefficients are used. Results are also shown in Table 26. SO₄ accounts for 56% of the fine fraction concentrations. Crustal components account for

85% of the coarse fraction. Predicted and observed total concentrations agree to within 15%.

Another set of regressions is used to determine whether the factors identified in one size fraction might serve as tracers in the other fraction. Fine and coarse concentrations were summed (to total mass of PM-15) and then regressed against fine Al, S, and Pb and coarse Al, S, Cl, Ca, and Cu concentrations at each site. Estimated coefficients (with $p < 0.05$) and apportionments are shown in Table 27.

TABLE 27. REGRESSION COEFFICIENTS AND SOURCE APPORTIONMENTS FOR COMBINED SIZE FRACTIONS IN ST. LOUIS

element and -source class--	-estimated coefficients- -average-	---range----	no. of sites	average observation (ng/m^3)	-apportionment- concn, percent ($\mu\text{g}/\text{m}^3$) (%)
fine Al (crustal)	9.4	-11.4 - 31.5 ¹	5	119.4	1.1 2.9
fine S (sulfate)	5.1	4.3 - 7.3 ²	10	2602.6	13.3 34.0
fine Pb (vehicles)	6.2	-5.2 - 21.9 ³	10	461.3	2.9 7.4
coar. Al (crustal)	14.0	7.2 - 17.8 ⁴	10	914.1	12.8 33.0
coar. Cl (roadsalt)	5.3	3.2 - 9.3 ⁵	5	245.2	1.3 3.3
coar. Ca (crustal)	2.2	0.9 - 3.8 ⁵	10	2269.2	5.0 12.9
constant (unexpl)	3505.2	2197.2 - 3874.0	5	na	2.2 5.7
R ² /total	0.54	0.48 - 0.88	10	40300.0	38.5 100.0

¹<0 at sites 2 and 9

²site 4=7.4; site 2=5.9; others=4.7

³<0 at sites 5 and 9; others=8.8

⁴site 1=9.5; site 5=7.2; others=15.3

⁵sites 7 and 8=0.9; others=2.5

In the combined regressions, coarse S and Cu are significant at only 3 sites. In comparison with results obtained using separate size fractions, the fine Al factor decreases from 3 to 1 g/m^3 , probably due to increases of the coarse Al factor (from 10.3 to 12.8 $\mu\text{g}/\text{m}^3$). The fine Pb factor decreases from 3.9 to 2.9 $\mu\text{g}/\text{m}^3$, while the Cl factor increases from 0.9 to 1.3 $\mu\text{g}/\text{m}^3$. The S and Ca apportionments are similar to that obtained using separate fractions.

The MLR technique provides an indication of particle compositions. For example, the average SO_4 coefficient of 5.1 is greater than the stoichiometric ratio of 4.1 for ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. Assuming the S measurements are unbiased, this indicates that additional material, probably water, is associated with SO_4 .

4.2 Receptor Modeling in Philadelphia

Monthly average apportionments for Philadelphia are estimated by the multiple linear regression method. Estimated coefficients and apportionments using the monthly average elemental concentration are listed in Table 28. These regressions explain 50-90% of the variance of fine and coarse fraction concentrations. Negative apportionments and apportionments derived from statistically insignificant coefficients in the table probably have little, if any, meaning.

In the fine fraction, S is the only element significant at all three sites, accounting for 52-65% of particle concentrations. At the Clarksboro and Airport sites, K accounts for 15-25% of particle concentrations. Other fine fraction elements have either insignificant coefficients or small effects. K may be a tracer for fertilizers from agricultural activities.

In the coarse fraction, Al is the only significant predictor at all three sites, accounting for 12-18% of the coarse fraction mass. Ca is significant at the Airport and Camden sites, accounting for 22-32% of the average concentration. The total crustal component (Al plus Ca) accounts for 50% and 34% of the coarse fraction concentration at the Airport and Camden sites, respectively. S is a significant

TABLE 28. REGRESSION COEFFICIENTS AND APPORTIONMENTS FOR SEPARATE SIZE FRACTIONS IN PHILADELPHIA

-----fine fraction-----						-----coarse fraction-----					
ele-	-estimated-	mean	-apportion-			ele-	-estimated-	mean	-apportion-		
ment	coef.	error	obser	conceq	pct.	ment	coef.	error	obser	conceq	pct.
			(ng/m ³)	(μg/m ³)	(%)				(ng/m ³)	(μg/m ³)	(%)
Airport Site											
Al	21.5	19.1	23.2	0.5	1.9	Al	3.8*	1.5	379.0	1.4	18.2
S	4.0*	0.3	3742.7	15.0	55.6	P	-15.2	31.7	22.0	-0.3	-4.2
K	86.5*	24.8	76.8	6.6	24.7	S	4.5	3.9	171.0	0.8	9.7
Ca	71.4	44.0	41.4	3.0	11.0	Cl	1.2	2.6	75.6	0.1	1.1
Cu	565.9*	172.1	0.1	0.1	0.2	Ca	8.4*	3.5	304.3	2.6	32.2
Sn	437.3*	140.9	2.0	0.9	3.2	V	-9.5	78.5	5.4	-0.1	-0.6
Pb	-6.0	7.0	213.0	-1.3	-4.7	Fe	2.2	3.0	359.6	0.8	10.0
Cqn	1845.3	2072.9	na	1.8	6.9	Pb	-44.2*	21.4	42.4	-1.9	-23.6
R ² /total	0.89	26935	26	100.0		Cqn	1821.3	1185.8	na	1.8	23.0
						R ² /total	0.74	7932	3.8	100.0	
Camden Site											
Al	41.7	27.0	33.3	1.4	4.8	Al	2.6*	1.1	547.5	1.4	12.1
S	3.9*	0.5	3857.8	15.0	51.6	P	8.8	28.2	29.7	0.3	2.2
K	9.5	16.7	97.6	0.9	3.2	S	10.3*	3.8	233.7	2.4	20.5
Ca	134.1+	73.5	39.5	5.3	18.2	Cl	3.7*	1.7	92.5	0.3	2.9
Cu	-670.6*	255.3	0.7	-0.5	-1.6	Ca	7.1+	3.6	358.9	2.5	21.7
Sn	-92.4	190.2	3.8	-0.4	-1.2	V	188.1*	67.8	7.5	1.4	12.0
Pb	14.1	12.7	246.7	3.5	11.9	Fe	1.0	5.1	489.7	0.5	4.2
Cqn	3020.3	3602.5	na	3.0	10.4	Pb	-13.2	18.6	54.2	-0.7	-6.1
R ² /total	0.8	29132	28.3	100.0		Cqn	467.8	1384.1		0.5	4.0
						R ² /total	0.85	11746	7.2	100.0	
Clarksboro Site											
Al	-28.3*	11.8	18.4	-0.5	-2.0	Al	4.7*	1.2	293.9	1.4	17.4
S	4.3*	0.2	3857.8	16.6	64.7	P	69.8*	19.0	25.7	1.8	22.6
K	68.1*	17.0	55.9	3.8	14.9	S	2.6+	1.5	260.6	0.7	8.5
Ca	66.3	50.1	20.6	1.4	5.3	Cl	9.1*	2.3	40.7	0.4	4.7
Cu	74.9	70.9	0.1	.0	.0	Ca	-6.0	4.8	180.5	-1.1	-13.7
Sn	2.6	54.6	4.7	.0	.0	V	83.9	61.2	4.1	0.3	4.3
Pb	0.7	7.8	134.2	0.1	0.4	Fe	7.6	5.4	241.5	1.8	23.1
Cqn	4627.9	1321.7	na	4.6	18.1	Pb	17.8	22.9	26.4	0.5	5.9
R ² /total	0.95	25620	26.0	100.0		Cqn	-673.0	828.7	na	-0.7	-8.5
						R ² /total	0.85	7932	3.7	100.0	

* denotes $p < .05$ + denotes $0.5 < p < .10$

predictor at Camden, but marginally at Clarksboro, accounting for 9-21% of the average concentration. Cl is significant at the Camden and Clarksboro sites, accounting for 3-5% of the concentration. V accounts for 12% of coarse concentrations at the Camden site. V may be a tracer for oil and refineries (Olmez and Gordon, 1985).

A second set of regressions is used to determine whether the factors identified above might "cross" size fractions. Summed fine and coarse fraction mass (PM-10) at each site are regressed against fine Al, S, and Ca and coarse Al, P, Cl, and V concentrations.

Estimated coefficients and apportionments are shown in Table 29. In

TABLE 29. REGRESSION COEFFICIENTS AND APPORTIONMENTS FOR COMBINED SIZE FRACTIONS IN PHILADELPHIA

element	-----Airport Site---				-----Camden Site----				---Clarksboro Site---			
	estimate	-apportion-	coef	err	estimate	-apportion-	coef	err	estimate	-apportion-	coef	err
			conce	pct.		conce	pct.			conce	pct.	
			($\mu\text{g}/\text{m}^3$)	(%)		($\mu\text{g}/\text{m}^3$)	(%)			($\mu\text{g}/\text{m}^3$)	(%)	
fine Al	-13	23	-0.3	-0.8	73+	42	2.4	6.0	5.7	16	0.1	0.3
fine S	3.7*	0.4	13.8	39.8	4.1*	0.6	15.8	38.7	4.5*	0.2	17.4	51.8
fine Ca	164*	51	6.8	19.5	21	85	0.8	2.0	135*	67	2.8	8.3
coar Al	11*	2	4.3	12.3	6*	2	3.1	7.5	3.8*	1.4	1.1	3.3
coar P	-86	75	-1.9	-5.4	67	87	2.0	4.9	82*	39	2.1	6.3
coar Cl	-7.5	8.5	-0.6	-1.6	-1.0	7.4	-0.1	-0.2	3.3	6.0	0.1	0.4
coar V	534*	193	2.9	8.3	593*	237	4.4	10.9	198+	144	0.8	2.4
Con	3303	3317	3.3	9.5	329	5020	0.3	0.8	4703*	2499	4.7	14.0
R ² /TOTAL	0.89	28.4			0.84	28.9			0.94	29.1		
TOTAL OBSERVED	34.8				40.9				33.5			

* denotes $p < .05$

+ denotes $0.5 < p < .10$

the combined regressions, only fine S and coarse Al are significant predictors at all three sites, accounting for 39-52% and 3-12% of PM-10 concentrations, respectively. The V contribution is 2-11%. The coefficient for S is 3.7, 4.1, 4.5 at the 3 sites, which is close to the stoichiometric ratio of 4.1 for $(\text{NH}_4)_2\text{SO}_4$.

4.3 Discussion and Summary

Receptor methods are useful only for the apportionment of those sources that have distinct composition and are predominantly of local origin, e.g., vehicles, incinerators, metal processing industries, and some oil-related sources. Receptor models do not separate local from regional sources that have similar elemental composition.

According to the multiple linear regression, 56% of the fine fraction and 34% of the total PM-15 levels in St. Louis are due to SO_4 . Previous studies (Dzubay, 1980) using summer data only, attributed a greater percentage to SO_4 (59 to 84% of the fine fraction). This could be due in part to higher transformation rates in the summer. Apportionments of other sources are similar to the previous studies. Crustal sources account for 85% of the coarse fraction and 46% of PM-15. Other sources tentatively identified include road salting, industrial emissions and incineration. The MLR model explains 50-90% of the variance of particle concentrations and indicates S, Ca and Cu are stable tracers.

In Philadelphia, the MLR approach indicates that SO_4 accounted for 52-65% of fine concentrations, and 39-52% of PM-10 concentrations. Crustal components account for 30-50% of the coarse fraction; oil and/or refinery sources (V) account for 2-11% of PM-10 concentrations;

vehicular sources may contribute 8-15% of PM-10. The identification of other factors is more speculative. Incineration (Cu) may account for 5-8% of fine fraction concentrations; and crustal or fertilizer sources (P, K) may compose 6-25% of particle concentrations.

MLR results indicate that the mass loading factor of elemental S is 5.1 in St. Louis and 4.1 in Philadelphia. The stoichiometric factor for $(\text{NH}_4)_2\text{SO}_4$ is 4.1; thus, in St. Louis, the sulfur component may have carried additional matter, perhaps water.

SECTION 5

MIXED MODELS

5.1 Introduction

With a few exceptions, statistical (receptor) and physical simulation (dispersion) models remain separate approaches in air quality modeling. To provide more accurate results, a "mixed model" was developed that incorporates features of both dispersion and receptor modeling.

In some respects, the mixed model described here resembles the "inverse" dispersion model and state-space approaches. In the inverse dispersion model problem, source emissions (rather than ambient concentrations) are predicted using ambient observations (Yamartino, 1984; Tombach, 1982). The mixed model differs in that multiple pollutants, source compositions and prior information are considered. In the state-space formulation, concentrations and some model parameters are estimated by reducing the advective-diffusive equation to linear difference equations evolving in time and using a Kalman filter (Desalu et al., 1974; Seinfeld et al., 1973). In contrast, the mixed model uses a static approach which is oriented to medium and long term particle apportionment, e.g., 12-hour samples collected for several weeks or months. The static approach permits a simpler numerical solution.

5.2 Mixed Model Formulation

A detailed description of a mixed model is given by Batterman (1986). Here we briefly summarize the major features of the model.

The model consists of several components. First, a dispersion model is used to calculate transfer coefficients. These coefficients indicate the contribution of local emission sources to receptors for the meteorological conditions during the sampling period. The Particle Episodic Model (PEM) (Rao and Stevens, 1985) is used with optimized dispersion parameters. Second, predictions of mass and elemental concentrations at receptor sites are made using the transfer coefficients and "prior" information. The latter includes the elemental composition and the particle emission rate of sources. Spatial and temporal aggregation is used to reduce the number of unknowns and simplify the estimation problem. Third, the prior information--emission rates and source compositions--is revised so that predicted mass and elemental concentrations best correspond to ambient measurements. Measurements collected at all receptor sites are used. Linear Bayesian estimates are used to correct for missing data. As the distributions of the parameters are unknown, a parametric approach is used in which range of uncertainties and covariances are selected. The primary outputs of the model are "posterior" estimates of emission rates and elemental compositions. Apportionments are derived as the product of the estimated emission rates and the transfer coefficients.

Observed ambient elemental concentrations are considered to be the sum of local and regional components, and an error term

$$C(i,k,t) = L(i,k,t) + D(k,t) + V(i,k,t) \quad (2)$$

where $C(i,k,t)$ is the observed concentration of element k observed at

site i and time t ; $L(i,k,t)$ is the contribution from local sources, $D(k,t)$ is the mean regional component of element k at time t which is assumed to be constant in space on the urban scale; and $V(i,k,t)$ is model and measurement error. The background component may be determined in several ways, e.g., using levels observed at an isolated upwind monitoring site.

The local component of mass and elemental concentrations is the sum of contributions from local sources

$$L(i,k,t) = \sum_j T(i,j,t) S(j,k) Q(j,t) \quad (3)$$

where the transfer coefficient $T(i,j,t)$ is the concentration produced at receptor i due to unit emissions from source j at time t . $T(i,j,t)$ represents the dispersive and advective effects of the atmosphere between the source and the receptor as well as particle deposition, settling and transformation processes. The source composition $S(k,j)$ is the mass ratio of emissions of element k to total particle emissions of source j . The source strength $Q(j,t)$ is the total particle emission rate of source j at time t . Secondary pollutants such as SO_4 , produced by the oxidation of gaseous SO_2 emissions may be modeled by modifying either the source composition or the transfer coefficient.

The optimization selects emissions $Q(j,t)$ and source compositions $S(j,k)$ of local sources to best match observed concentrations. The uncertainty for these parameters is explicitly specified. Emissions and compositions are permitted to vary within the corresponding range of the assumed uncertainty.

To reduce the number of unknown parameters, local contributions in Eq. (3) are modeled using three cases, (1) for sources with known compositions, (2) unknown and unique compositions, and (3) unknown and common compositions. The total contribution from local sources is the sum of the predictions of the three cases. In addition, sources are spatially aggregated. Nearby sources in the same source class are combined and emissions and compositions are estimated for the source group.

The time dependence of emissions is removed by incorporating the emission schedule in the transfer coefficients. Emission schedules are derived from emission inventories. Thus, a "static" approach may be used, employing long term pollutant observations and predictions. This further reduces the problem dimension, and takes advantage of the increased accuracy of long term dispersion model predictions. Concentrations may be classified by (1) wind direction; (2) stability class; (3) season; (4) time of day and day of week; (5) the pollutants themselves, e.g., the presence of unusually high pollutant concentrations may indicate an influx of regional pollutants; and (6) precipitation or other meteorological events. Prior information for particle emissions are based on data from the source inventory; prior source compositions use the best available values (Core et al., 1985).

5.3 Application and Results

The mixed model is evaluated using one month of data from the Philadelphia study. Results are briefly summarized here.

For distributed (area) sources, estimated emissions and apportionments increase from the priors (using the emission inventory

estimate) in the coarse fraction, but decrease in the fine fraction. Minor point source emissions change most (proportionally) at the peripheral sites (Clarksboro and Airport), increasing in the fine fraction and decreasing in the coarse fraction. Mobile source contributions decrease in both size fractions. For point sources, estimated coarse fraction emissions from oil power plants and refineries are higher than the priors; emissions from coal power plants are lower. Coal emissions decrease in both size fractions. Incinerator emissions double in the coarse fraction. Emissions from metal/smelter and chemical sources do not change significantly from the prior, and reflect large uncertainties.

Results are assessed by comparing particle observations and dispersion model predictions using the estimated emission rates and optimized dispersion parameters. In the fine fraction, these predictions had higher correlation than dispersion modeling using the standard parameters (see Section 3). Coarse fraction correlations increased, but remain near zero. The mixed model marginally improved the spatial agreement. Coarse fraction particle modeling remains problematic, possibly due to inaccurate emission schedules for area sources. The evaluation is preliminary; application to other data sets would help to confirm the results.

5.4 Conclusion

Mixed models may be useful in a number of applications. First, these models can reconcile different apportionments generated by simulation and receptor models. Second, the results provide a check on the accuracy of the source inventory. Third, the appropriateness

of source compositions may be assessed. Fourth, it may be possible to identify unknown sources, detect locations of accidental releases, etc. Fifth, the approach forces the explicit quantification of uncertainty.

Results of the mixed model are always equal or superior to apportionments obtained by separate models because all information is used. With limited observations, the physical (dispersion) model solution will dominate; with very uncertain priors and many observations, the statistical (receptor) model apportionment will be controlling. In the case study, the physical model dominated due to the diversity of sources and the relatively few observations available. Additional monitoring sites and better source information would help to separate the many sources in the Philadelphia area.

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